

DEVELOPMENT OF VULCANIZABLE
ELASTOMERS SUITABLE FOR
USE IN CONTACT WITH
LIQUID OXYGEN

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PREPARED BY:

Paul D. Schuman

Paul D. Schuman, Senior Research Chemist

APPROVED BY:

Eugene C. Stump

Eugene C. Stump, Project Director

FOREWORD

This report was prepared by Peninsular ChemResearch, Inc., under Contract NAS8-5352, "Development of Vulcanizable Elastomers Suitable for Use in Contact with Liquid Oxygen," with the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, Material Division of the George C. Marshall Space Flight Center with Dr. William Hill acting as the Contracting Officer's Technical Representative.

Other personnel who have contributed to this research were Drs. T. W. Brooks and D. A. Warner, Senior Research Chemists; Geraldine Westmoreland, Carl Daffin, and Harris Meadows, Research Chemists; Beatrice Gianinni and R. Harrell, Technicians. Drs. George B. Butler and Paul Tarrant are acting consultants. In addition, Dr. Wallace Brey of the University of Florida carried out and interpreted NMR spectral analyses, and Dr. R. Hanrahan, also of the University of Florida, assisted in radiation induced polymerization studies.

ABSTRACT

In attempts to copolymerize trifluoroacetaldehyde with perfluoropropylene epoxide, a new reaction was found which yields previously unknown esters having the structure $R_f\text{COOCHFCF}_3$. Polymer composition curves for the fluorocarbon vinyl ethers with vinylidene fluoride have been prepared. A $\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2/\text{CF}_3\text{NO}$ "nitroso" polymer has a T_g of -1 to -5° . Attempts to prepare a polyester using trifluoroacetaldehyde hydrate as the diol have not been successful. Some preliminary experiments have been run to determine the feasibility of preparing a poly(thioperoxide). Attempts to exhaustively dechlorinate $\text{CF}_3\text{OCCl}_2\text{CFCl}_2$ did not yield $\text{CF}_3\text{OC}\equiv\text{CF}$. Reaction of $\text{CF}_3\text{OCFC1CFC1OCF}_3$ with zinc results in decomposition. T_g of a $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$ (PVM/ $\text{CF}_2=\text{CH}_2$) copolymer containing 14.6 wt. % PVM was found to be -55 to -57° . Some preliminary experiments have been run to determine the feasibility of preparing a fluorocarbon polyperoxide. An elastomeric copolymer of $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$ has been prepared. A $\text{CF}_3\text{OCF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$ copolymer containing 83.8 mole percent $\text{CF}_2=\text{CH}_2$ was found to be LOX compatible. Tensile strength and elongation of $R_f\text{OCF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$ above and below T_g suggest usable mechanical properties below T_g . Preliminary attempts have been made to plasticize and determine the effect of plasticization on physical properties of a $\text{CF}_3\text{OCF}=\text{CF}_2/\text{C}_2\text{F}_4$ copolymer. The fluorocarbon diketone, $(\text{CF}_3)_2\text{CFCO}(\text{CF}_2)_3\text{COCF}(\text{CF}_3)_2$, has been prepared.

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INTRODUCTION

This report describes work carried out during the fourth year of Contract NAS8-5352. It is preceded by thirty monthly reports, eleven quarterly reports, and three annual summary reports.

Past efforts and the ultimate goal of this project, to develop elastomeric polymer systems which are vulcanizable and suitable for use in contact with liquid oxygen, make it quite evident that the required systems will be polymeric systems containing large proportions of fluorine and/or chlorine.

Due to the lack of data concerning low temperature properties of halocarbon polymers, in particular those of the fluorocarbons, it has been necessary, at least initially, to attempt to relate structural features of the hydrocarbon and available halocarbon polymer systems which enhance low temperature properties. Obviously, the desired low temperature properties which may be directly related to a polymer's usefulness at cryogenic temperature are mechanical properties. Unfortunately, a thorough search of the literature reveals little information in this area. In lieu of this information, other thermal properties which are more readily available in the literature have been chosen for comparison. These properties are the crystalline melting point (T_m) and the glass transition temperature (T_g). A correlation between T_m and T_g has been recognized¹⁻³ which permits an approximation of T_g from T_m a knowledge of the more readily available T_m . Thus, for symmetrical crystalline polymers as poly(ethylene), $T_m = T_g$, and for unsymmetrical crystalline polymers as poly(propylene), $T_m = 1.4 T_g$ in °K.

Unfortunately, the usefulness of this relationship is limited for the present investigation since non-crystalline polymers, such as the elastomers desired in this work, melt over a considerable range allowing the possibility of only an extremely crude, if any, approximation of T_g from the melting range. It would thus appear that any extensive correlation of polymer properties with structure without resorting to actual temperature-property-structure determination must necessarily rely on literature references to T_g data. The relationship

(1) R. R. Boyer, "Changements de Phases," p. 383, pub. by Soc. de Chemie Physique, Paris, 1952.

(2) R. G. Beaman, J. Polymer Sci., **9**, 472 (1953).

(3) Jenkel, Kolloid-Z., **130**, 64 (1953).

of glass transition temperatures to mechanical properties of a polymer is not known at this point, but in the present investigation a good correlation between T_g and modulus of rigidity and also the Clash-Berg stiffness test has been obtained for the copolymer system, $\text{CH}_2=\text{CF}_2/\text{CF}_3\text{OCF}=\text{CF}_2$. Boyer⁴ has, in addition, proposed a possible correlation between the area under the curve of transitions occurring below T_g and room temperature impact strength.

Rogers and Mandelkern⁵ have found that by increasing the chain length of the alkyl group in poly(alkyl methacrylates from CH_3 to C_9H_{19} , T_g is reduced about 170° . On further increasing the length of the side group to $\text{C}_{18}\text{H}_{37}$, no T_g was detected (analysis by linear expansion). However, extrapolation of the data as done by Shen and Eisenberg,⁶ suggests a T_g of -100° for poly(octadecylmethacrylate). Somewhat surprising also⁸ is the lowering of T_g of poly(styrene) from 105° to -65° by increasing the chain length of a p-alkyl group to C_{10} . This is a decrease of 170° . These low values were terminal values on a plot of a homologous series and did not represent minima. This would indicate that no side chain crystallization is occurring as observed by Lal and Trick⁷ for a series of vinyl ethers which exhibited a minimum T_g at $\text{R}=\text{C}_8$.

These data tend to support our present view concerning the desirability of preparing fluorocarbon polymers having long pendent perfluoroalkoxy groups. In effect, the side chain is acting as a chemically bonded plasticizer. The effect this type of plasticization and also external plasticization has on physical properties of polymers below T_g is of particular interest in the present study.

Additional discussion concerning the effect of structure on polymer glass temperature is included in the First and Second Annual Reports on this contract.

(4) R. F. Boyer, Rubber Chem. and Tech., 36 (5), 1303-1421 (1963).

(5) S. S. Rogers and L. Mandelkern, J. Phys. Chem., 61, 985 (1957).

(6) M. C. Shen and Adi Eisenberg, NONR 233 (87) Tech. Rpt. No. 9, August 1, 1965.

(7) J. Lal and G. Trick, J. Polymer Sci., Pt. A, 2 (10), 4559-4572 (1964).

DISCUSSION

A. Polymers, Synthesis and Properties

Although our investigation thus far has, in general, been directed toward illucidation of the effect of structure on T_g , we realize that polymer glass temperatures were used as a matter of convenience and did not necessarily reflect possible useful mechanical properties below T_g .

A number of commercially available polymers have glass temperatures above their normal use temperature. Room temperature physical properties of polymers, such as poly(vinyl chloride), poly(methylmethacrylate), and poly(ethylene terephthalate), suggest degrees of glassiness below T_g .

In order to determine what effect pendent alkoxy chain length has on T_g , as well as physical properties below T_g , a number of fluorocarbon vinyl ethers were prepared. Using the method of Fritz, Moore, and Selman⁸ a number of vinyl ether copolymers ($R_f\text{OCF}=\text{CF}_2$) were prepared (Tables II and III) where R_f was CF_3 (MVE), C_2F_5 (EVE), C_3F_7 (PVE), C_4F_9 (BVE), and $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2$ (TO). In addition, a small amount of $(\text{CF}_3\text{O})_2\text{CF}=\text{CF}_2$ (PVM) was prepared (see Third Annual Report). The reactivity of the lower member vinyl ethers with vinylidene fluoride (VF_2) appear to be similar as indicated in Figure 1. Bulk polymerization of a monomer charge of 20 mole percent vinyl ether, at 800 atmospheres pressure, yields a copolymer containing between 10 and 17 mole percent vinyl ether. The reactivity of $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$ (PVM) with VF_2 , as expected, is less than that of the vinyl ethers. A similar monomer charge (20%) yields a copolymer containing about 2 to 3 mole percent PVM.

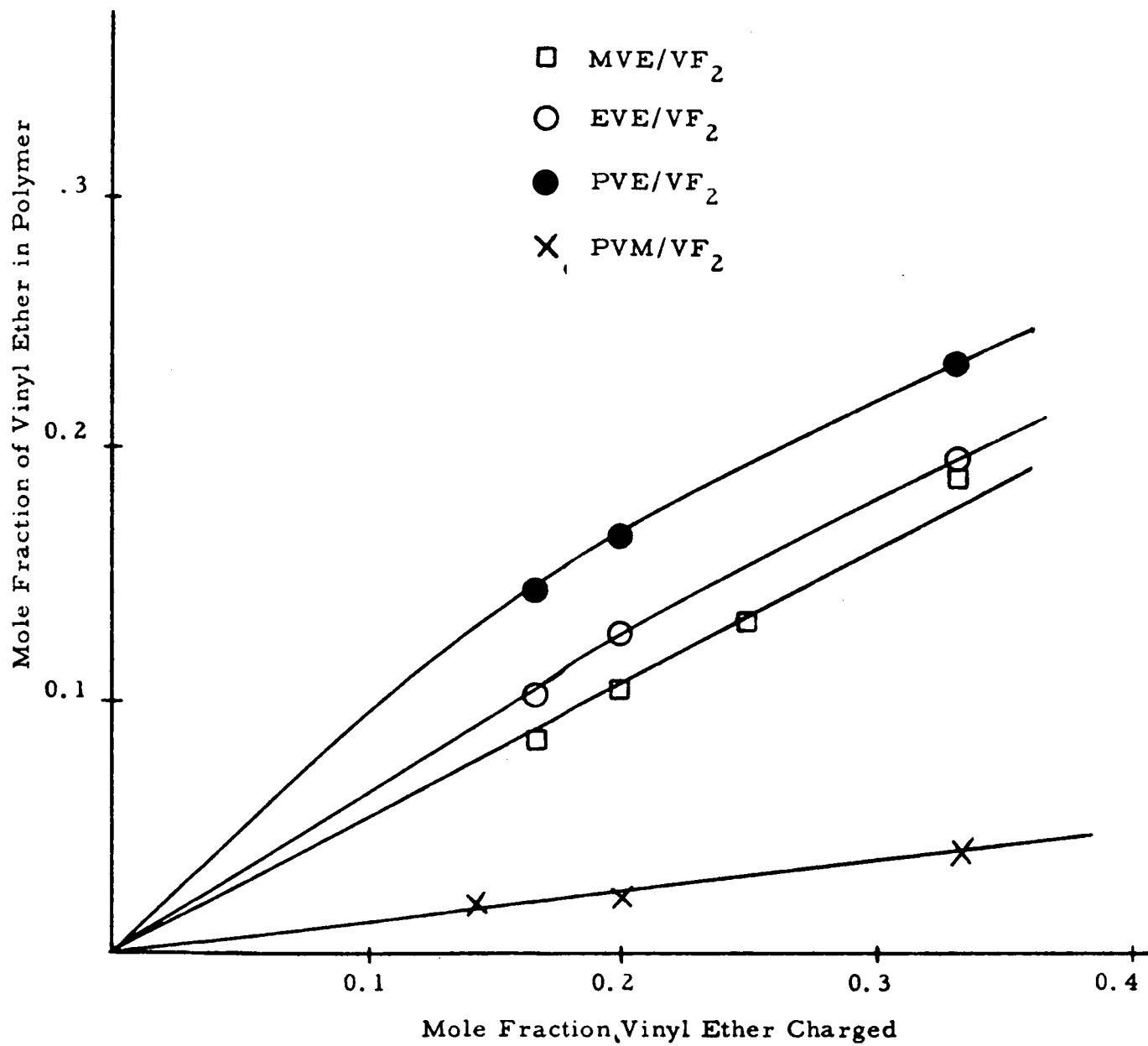
A copolymer of $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}=\text{CF}_2$ (TO) with VF_2 was prepared by reacting a 2.2 to 1 molar ratio of VF_2/TO at 1000 atm, using a free radical initiator. The resultant elastomeric polymer, 92P, Table II, contained 12.4 mole percent (56.9 wt. %) vinyl ether. The polymer was molded at 100° into a weak elastomeric film.

It will be interesting to compare the T_g and physical properties of this copolymer, which has a branched but flexible side chain with copolymers having a more rigid side chain like that of $\text{C}_8\text{F}_{17}\text{OCF}=\text{CF}_2$. This comparison will be of particular interest in view of the T_g data obtained

(8) C. G. Fritz, E. P. Moore, Jr., and S. Selman, U. S. Patent 3,114,778, December 17, 1966.

FIGURE 1

Copolymerization of Fluorocarbon Vinyl Ethers
with Vinylidene Fluoride
(Bulk polymerization at av. p of 800 atm.)



thus far on the fluorocarbon vinyl ethers (Table IV) which indicate little, if any, change in T_g for vinyl ethers having OCF_3 , OC_2F_5 , OC_3F_7 , and OC_4F_9 pendent groups. A plot of T_g vs wt. % VF_2 , from the data given in Table IV, shows considerable scatter but a straight line extrapolation indicates that the glass transition temperatures of poly(MVE), EVE, PVE, or BVE all lie between 0° and -16° .

Copolymerization of $\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2$ with CF_3NO at high pressure, as described in our Third Annual Report, yielded a copolymer which has a T_g of -1 to -5° . Thus far it has been found that the glass temperature of all fluorocarbon vinyl ether "nitroso" copolymers ($\text{R}_f\text{OCF}=\text{CF}_2/\text{CF}_3\text{NO}$) range between -7 and 1° . The last member prepared in this series, where $\text{R}_f=\text{C}_4\text{F}_9$, has some resilience, but is a weak gum at room temperature.

Preliminary thermal analysis of the PVM/ VF_2 , $(\text{CF}_3\text{O})_2\text{CF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$, copolymer (69), containing 14.4 wt. % PVM indicates a T_g of -55 to -57° .

Attempts to exhaustively dechlorinate $\text{CF}_3\text{OCCl}_2\text{CFCI}_2$ to obtain the new monomer $\text{CF}_3\text{OC}\equiv\text{CF}$ were not successful.

1. LOX Compatibility of Vinylidene Fluoride-Trifluoromethyl Trifluorovinyl Ether Copolymers

Two copolymer samples were submitted to the Materials Division for LOX compatibility tests. The results of these tests are summarized below.

<u>Sample</u>	<u>Monomers (mole %)</u>	<u>Test Results⁹</u>
		<u>Detonations/No. of Tests</u>
75P	$\text{CF}_3\text{OCF}=\text{CF}_2$ (12.5)/ $\text{CF}_2=\text{CH}_2$ (87.5)	5/17
90P	$\text{CF}_3\text{OCF}=\text{CF}_2$ (16.7)/ $\text{CF}_2=\text{CH}_2$ (83.3)	0/20
242-47	$\text{CF}_3\text{OCF}=\text{CF}_2$ (30)/ C_2F_4 (70)	0/16

It is surprising to find that copolymer 90P, containing a relatively large amount of vinylidene fluoride, is LOX compatible. The results of this test suggest a LOX compatibility limit of vinylidene fluoride in these copolymers to lie between 83.3 and 87.5 mole percent and further indicate the possible use of these elastomers in LOX systems.

The totally fluorinated plastic copolymer 242-47 was, as expected, also LOX compatible.

(9) Compatibility determined by a standard test method (MSFC 106B, "Testing Compatibility of Materials for Liquid Oxygen Systems," September 16, 1966) where a sample of film is immersed in liquid oxygen and struck with a 10 Kg-m force. Hydrocarbon polymers will detonate under these conditions.

2. Physical Properties of Some Fluorocarbon Vinyl Ether Copolymers

The tensile strength and elongation of several fluorocarbon vinyl ether-vinylidene fluoride copolymers was determined above and below their glass temperature (Table V). The data used in the preparation of these curves were obtained by determining hoop strengths between about -70° and room temperature. Unlike usual tensile tests, where the cross-head speed is constant ($\Delta L/\Delta T=C$), the data from which these figures were derived was obtained at constant rate of stress ($\Delta S/\Delta T=C$). Load rates were about $8-10 \text{ Kg/cm}^2/\text{min}$.

In Figure 2 are shown some typical stress-strain curves of a BVE/VF₂ (98P, 59.6 wt. % vinyl ether) copolymer as determined above and below T_g . The lower three curves, which show essentially no yield point, were run at temperatures above T_g . These curves are typical of rubber-like materials. The transition from a rubber-like material to a plastic is shown for the stress-strain curve run at -50° . This change in properties indicates T_g to lie between -50 and -20° . Calorimetric analysis of polymer samples of similar composition indicate T_g to be about -25° . These stress-strain curves are similar to those found for MVE/VF₂ copolymers.

Although only a limited amount of physical test data has been obtained thus far, it would appear that fluorocarbon vinyl ether-vinylidene fluoride copolymers have usable mechanical properties below their glass temperature. The change in properties noted in the stress-strain curves is not reflected in the elongation-temperature curve (Figure 3). No precipitous drop in elongation occurs at the glass temperature as might be expected for a polymer which is glass-like below T_g .

A series of additional tests were initiated in an attempt to determine the effect of polymer composition on the low temperature properties of MVE/VF₂ copolymers. The data obtained thus far are shown in Table V and a plot of this data showing the effect of polymer composition on tensile strength and elongation is shown in Figure 4.

The tensile strength and elongation of a MVE/C₂F₄ copolymer (~ 20 mole percent ether) was determined at 25° and -75° . This copolymer has a tensile strength of 462 Kg/cm^2 and an ultimate elongation of 13% at -72° (Table V).

3. Effect of Plasticization on Low Temperature Properties of a Tetrafluoroethylene-Trifluoromethyl Trifluorovinyl-Ether Copolymer

Some preliminary attempts have been made to plasticize and determine the effect of plasticization on physical properties of a CF₃OCF=CF₂(MVE)/C₂F₄(TFE) copolymer. The data obtained thus far are summarized in Table I and Figure 5.

FIGURE 2

Stress-Strain Curves for $C_4F_9OCF=CF_2/CF_2=CH_2$
Copolymer, 98F, Above and Below T_g

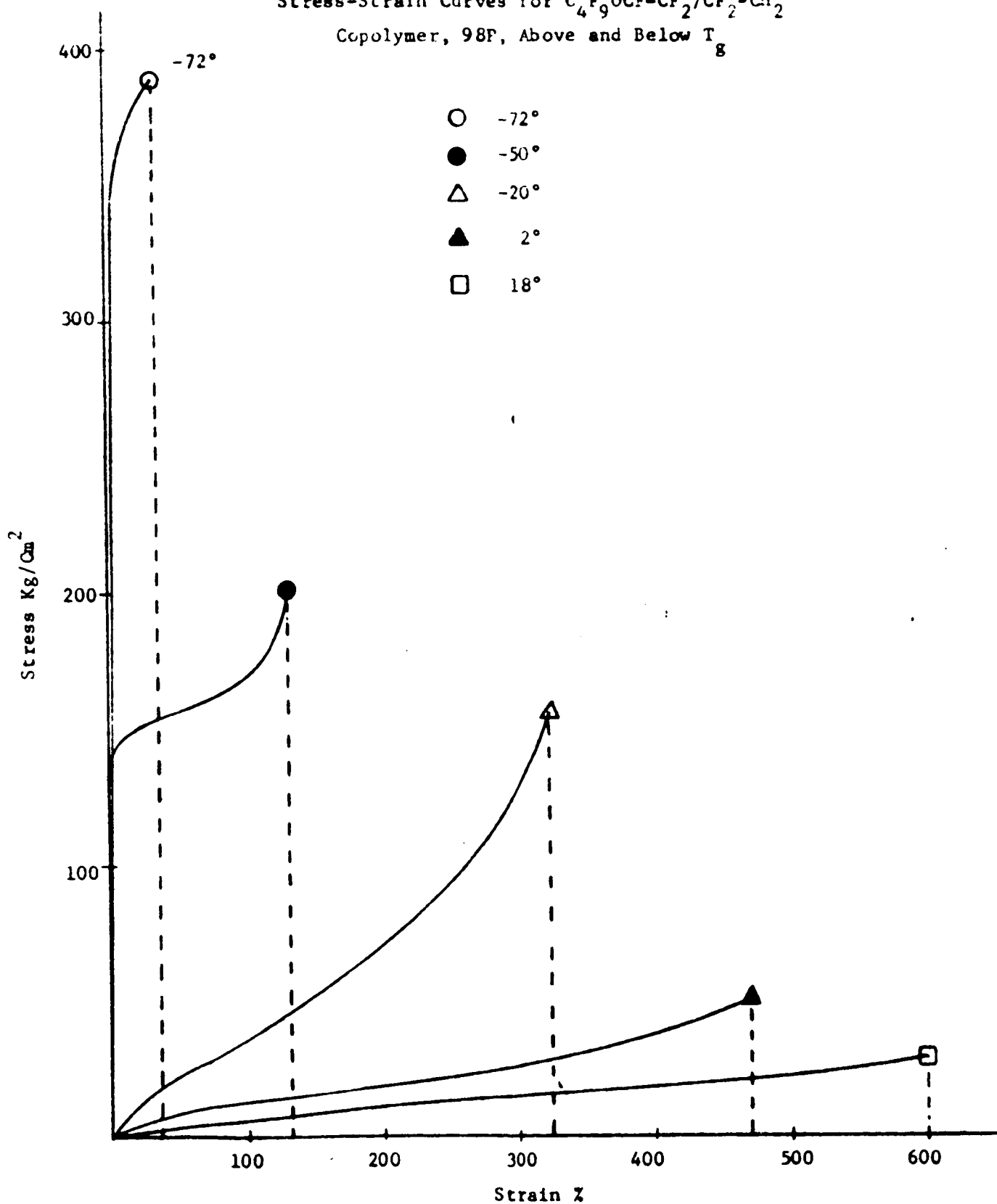


FIGURE 3

Elongation-Temperature Curve For
 $\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$ Copolymer 98P

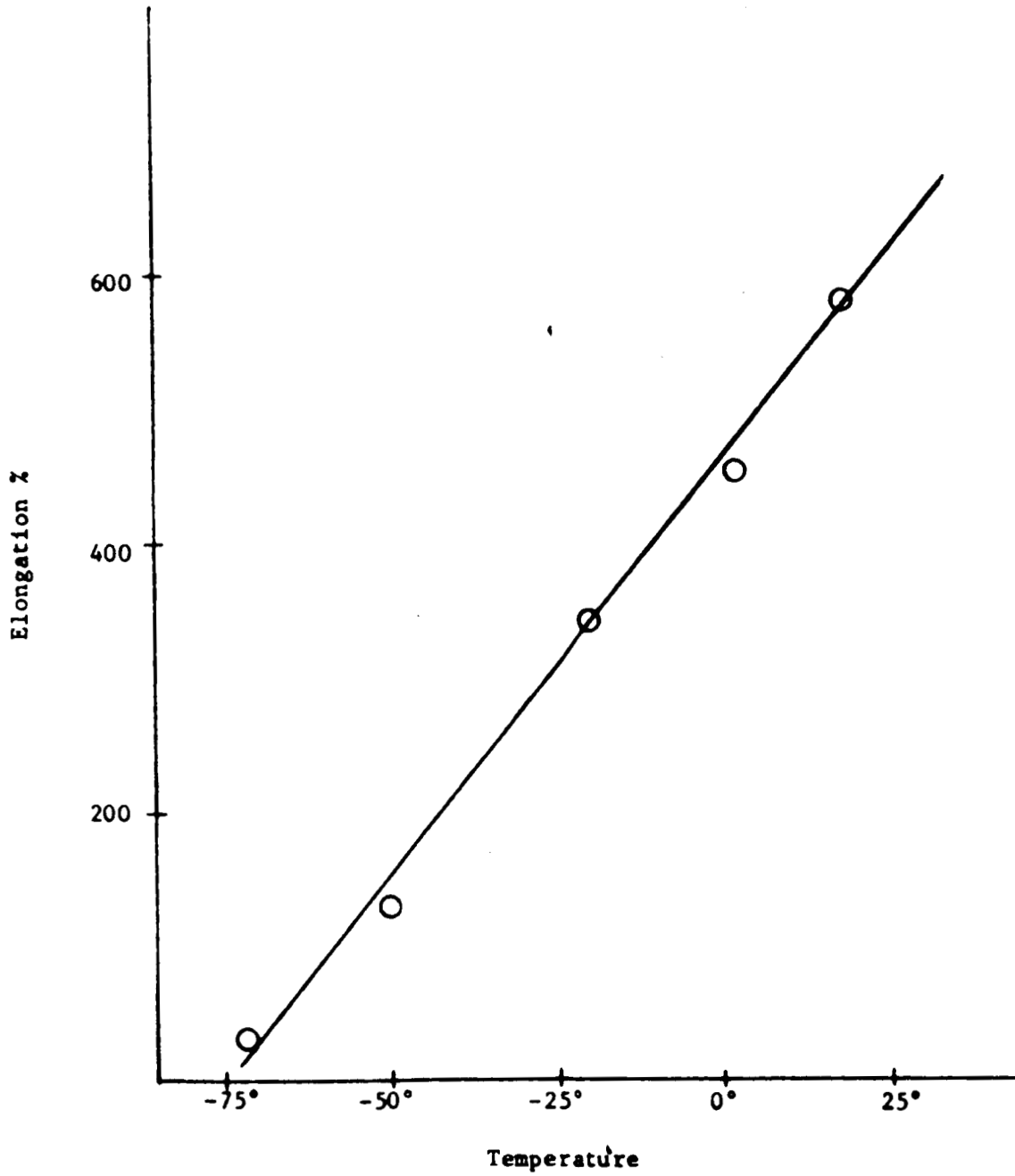


FIGURE 4

Effect of Composition on Copolymer Physical Properties

(Copolymer $\text{CF}_3\text{OCF}=\text{CF}_2/\text{CF}_2=\text{CH}_2$)

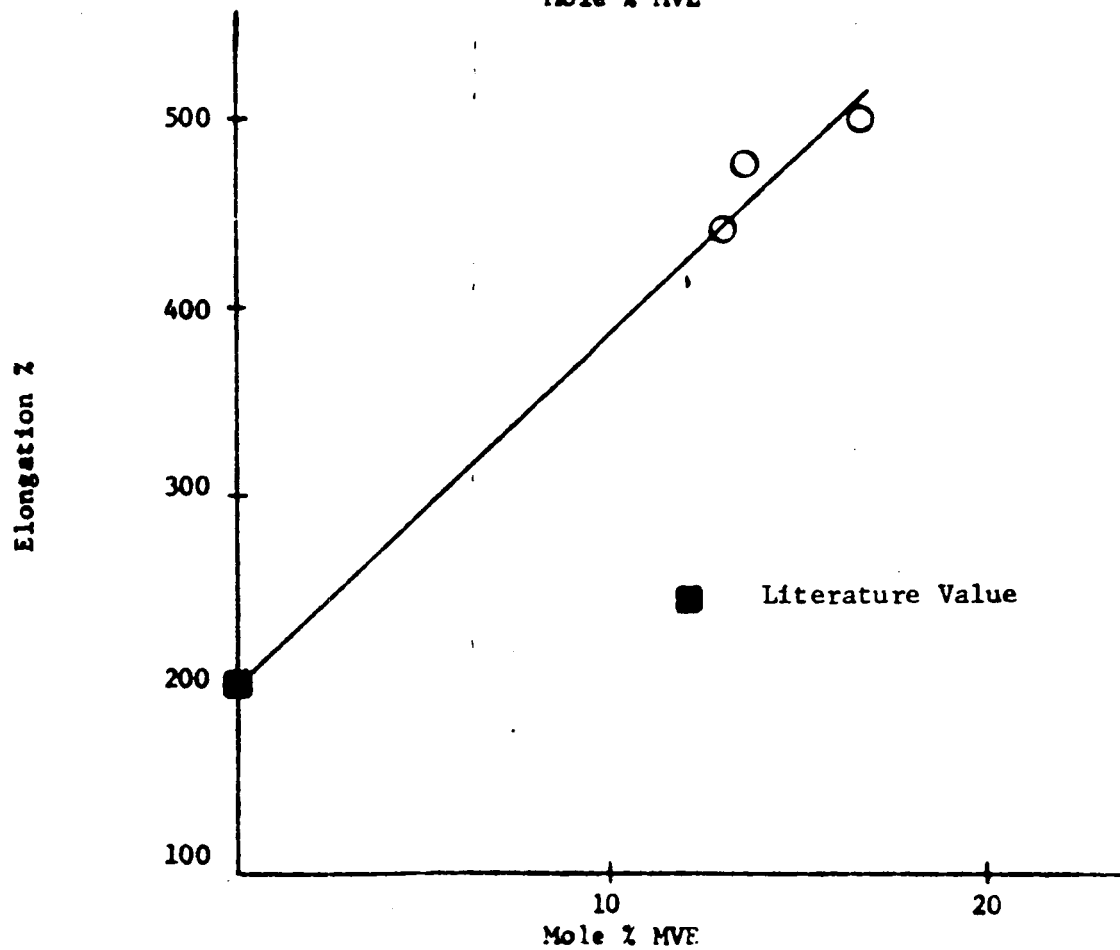
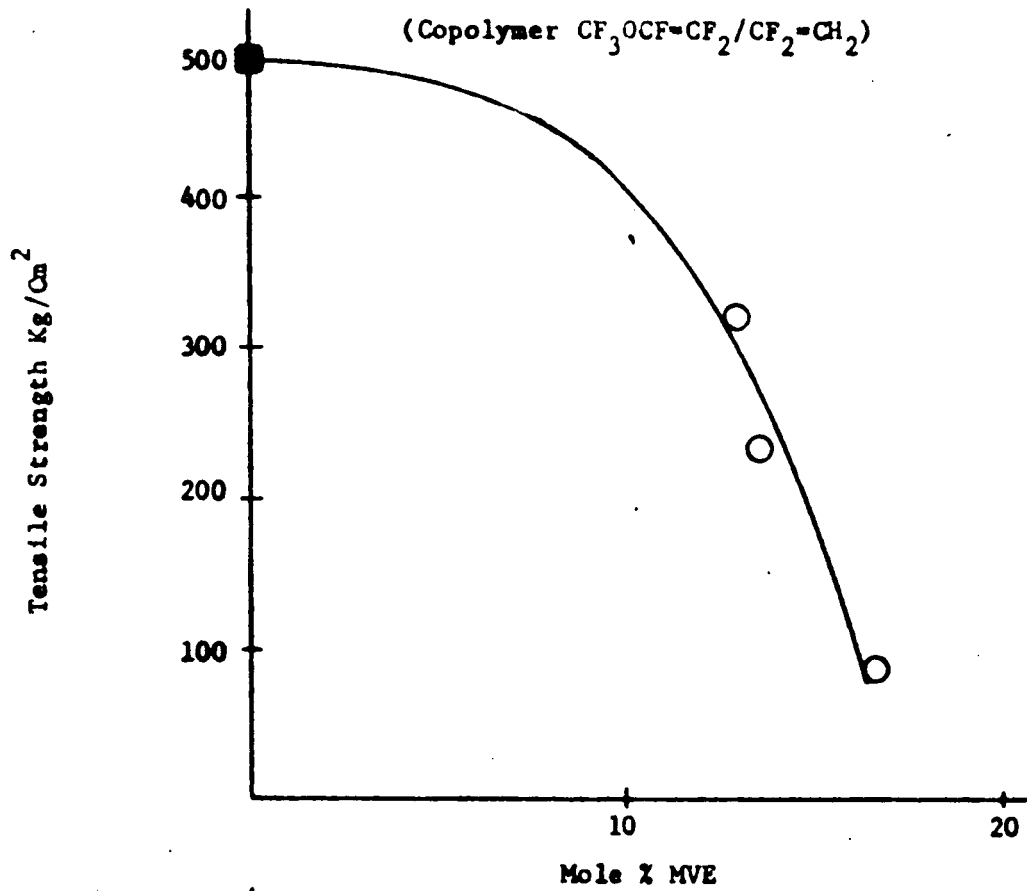
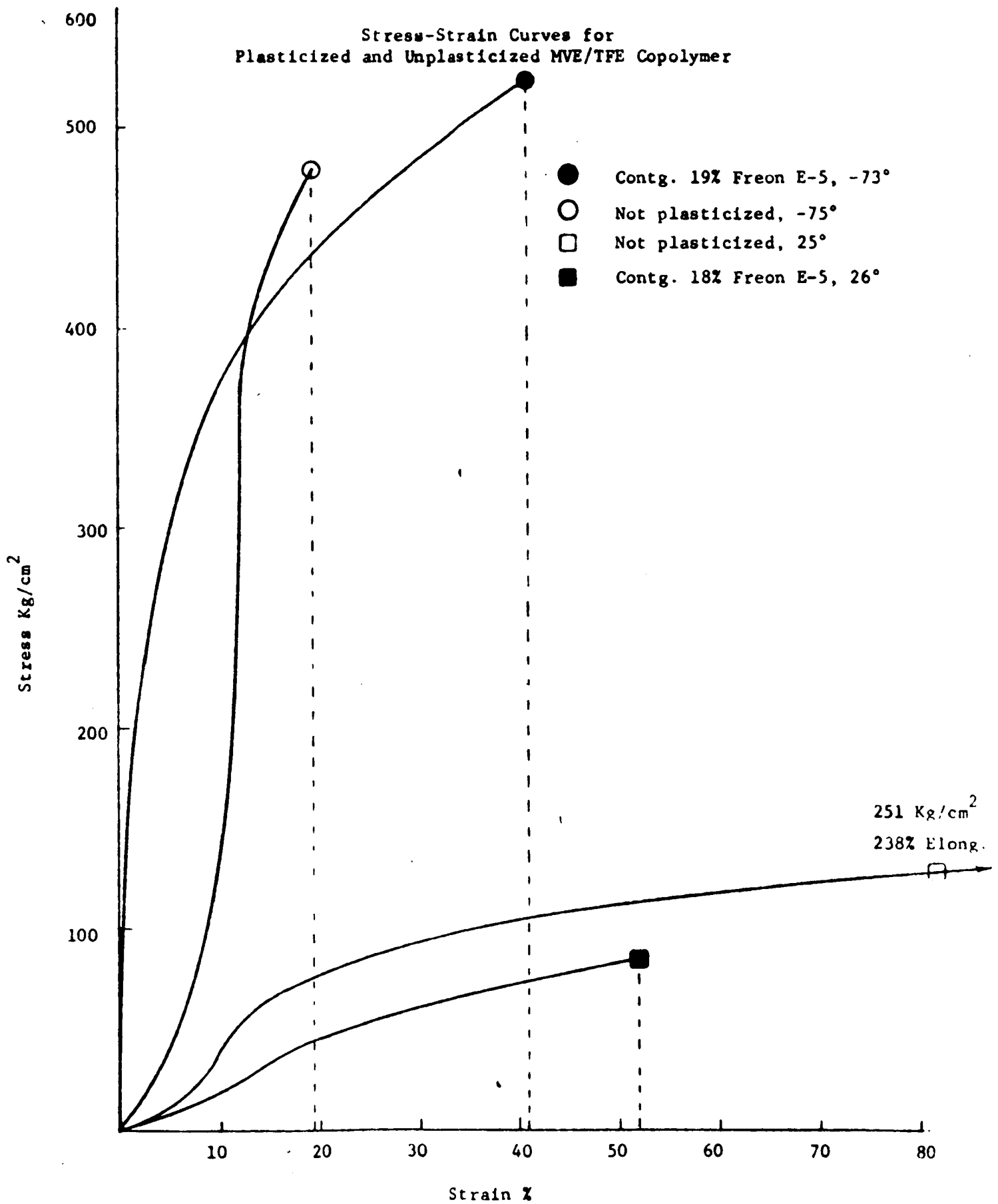


FIGURE 5

Stress-Strain Curves for
Plasticized and Unplasticized MVE/TFE Copolymer



As reported in the Third Annual Report of this contract, copolymers of MVE/TFE are plasticized by Freon E-5.¹⁰ The tensile samples were cut, measured, then immersed in boiling Freon E-5 for five minutes. After immersion the initially plastic film changed to a tough elastomeric film containing about 20% plasticizer. In these tests the amount of plasticizer absorbed or dissolved in the copolymer is considerably below that previously reported (67%, Third Annual Report). This difference is presumably due to copolymer composition. (An accurate analysis of these copolymers is difficult due to the similarity in carbon content of the two monomers and the difficulty in obtaining an accurate fluorine analysis.) The copolymer composition of 20% MVE in 315-18 is only a rough approximation based on the monomer charge and polymer yield.

Typical stress-strain curves for plasticized and unplasticized MVE/TFE copolymer 315-18 at room temperature and at -73° and -75° are shown in Figure 5. It is interesting and encouraging to note that plasticization is effective at -73°. Elongation is doubled and surprisingly there is also a small increase in tensile strength. A comparison of the plasticized and unplasticized copolymer tested at room temperature shows the effect of plasticization by the increased extension for a given stress but, in contrast to the low temperature tests, plasticization appears to drastically reduce the ultimate elongation.

TABLE I
Physical Properties of a Plasticized^a MVE/TFE Copolymer

Sample	% Plasticizer (Freon E-5)	Test Temp.	Tensile ^b Strength Kg/cm ²	Elongation %
1	17.7	25°	131	82
2	21.0	25°	122	84
5	18.3	26°	86	
3	19.8	-73°	522	43
4	19.1	-73°	527	41
6	0	-75°	475	19
7	0	25°	251	238

(a) Polymer sample 315-18 γ -ray initiated copolymerization of a 4:1 molar ratio of C_2F_4 (TFE)/ $CF_3OCF=CF_2$ (MVE) at -78°. Copolymer contained about 20 mole percent MVE.

(b) Load rates were about 7 Kg/cm²/min. Tensile specimen was plasticized by immersion of the precut sample in boiling Freon E-5 for five minutes. Plasticizer content was determined and tensile tests run immediately afterward.

(10) Freon E-5, $C_3F_7O[CF(CF_3)CF_2O]_4CFHCF_3$, E. I. duPont de Nemours and Company.

Since a rather crude means of addition of plasticizer was used, this loss in room temperature properties is more likely due to crazing or poor plasticizer distribution than to the presence of plasticizer in the copolymer. Proper plasticization should not only improve the room temperature properties, but should also improve upon the already improved low temperature properties.

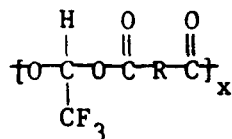
4. Attempted Preparation of a Polyester Containing $\text{CF}_3\text{CH}(\text{OH})_2$ as the Diol

In order to determine the feasibility of preparing a polyester from the hydrate of trifluoroacetaldehyde, an initial acylation was carried out in an attempt to confirm the findings of Husted, *et al.*¹¹ that the hydrate does react as a diol. Since the hydrate, as purchased, contains a considerable amount of water, ethanol and ethyl hemiacetal, a secondary objective of this acylation was to obtain the pure diol.

Refluxing the hydrate with acetic anhydride over a 30-hour period gave a low yield, about 20%, of the diacetate. An infrared spectrum of this compound is shown in Figure 6.

An initial attempt to prepare a polyester by reacting the diacetate with adipic acid and removing acetic acid as formed resulted in considerable carbonization and only a trace amount of tar. The reaction was carried out by heating the reactants to the reflux temperature of the diacetate ($151-152^\circ$) under a packed distillation column. As the reaction proceeded the reflux temperature dropped to 118° and acetic acid was removed until the temperature started to rise. The reaction proceeded very slowly with only a small amount of acetic acid removed in several hours. On refluxing overnight, carbonization occurred. An infrared spectrum of the trace amount of tar obtained showed a C-H stretching maximum at 3.4 microns, a carbonyl maximum at 5.85 microns, and maxima between 7 and 9 microns which do not correspond with those of adipic acid.

It would appear that some polyester was formed and that high molecular weight polyesters having the following structure might be obtained under milder conditions through use of a catalyst.

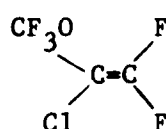
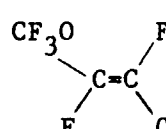


(11) D. R. Husted, A. H. Ahlbrecht, U. S. Patent 2,568,501, September 10, 1951.

In an attempted modification of this polyesterification reaction the trifluoroacetaldehyde hydrate and diethyl malonate were heated to reflux under a packed fractionating column. Initially, condensation appeared to be occurring. This was indicated by the presence of ethanol in the distillate. However, after an extended time at reflux only a small amount of ethanol was removed and little, if any, viscosity build-up was noted.

B. Attempted Dechlorination of $\text{CF}_3\text{OCFC1CFC1OCF}_3$

In our final attempt to prepare the elusive 1,2-bis(trifluoromethoxy)-difluoroethylene (DME) by reaction of the titled compound with zinc, the only identified olefinic product was PVM. A second major peak (11% of the GLC peak areas) which appeared most likely to be the expected DME has been found, by NMR analysis, to be composed of three isomeric compounds plus an unknown compound containing an OCF_3 group. This NMR data is given below with the chemical shifts for fluorine given with respect to CF_3COOH .

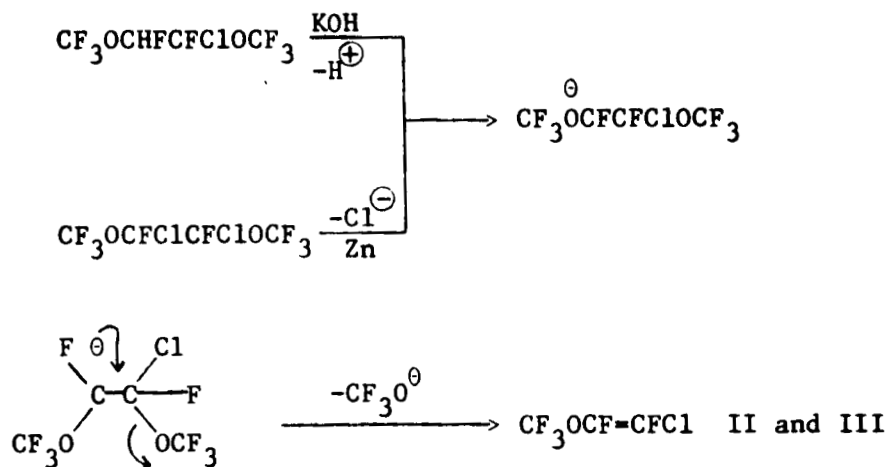
<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Assignment</u>
<div style="text-align: center;">  <p>(I, 45%)</p> </div>			
A-2	-15.6	$2^\circ \times 4.0$	CF_3O
E	+28.9	$2^\circ \times 49, 4^\circ \times 4.5$	CF cis to CF_3O
G1	+45.3	$2^\circ \times 49$	CF trans to CF_3O
<div style="text-align: center;">  <p>(II, 35%)</p> </div>			
A-3	-15.4	$3^\circ \times 4.3$	CF_3O
FH	+44.6	$2^\circ \times 121, 4^\circ \times 4.5$	CF gem to CF_3O
JK	+51.5	$2^\circ \times 121, 4^\circ \times 4.5$	CF cis to CF_3O

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Assignment</u>
		$ \begin{array}{c} \text{CF}_3\text{O} \quad \text{Cl} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{F} \quad \text{F} \end{array} $ (III, 9%)	
A-4	-14.7	2° x 5.4	CF ₃ O
C	+16.7	4° x 5, 2° x 43	CF gem to CF ₃ O
D	+26.3	2° x 43	CF trans to CF ₃ O

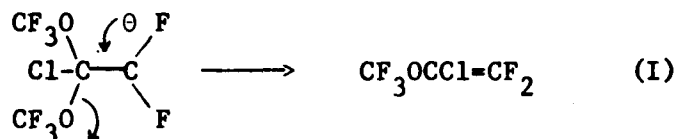
Unknown Component

A-1	-15.8	1°	CF ₃ O
B	+ 7.2	Multiplet	?

It is interesting to note that the three isomeric compounds I, II, and III are the same decomposition products found in attempts to dehydrochlorinate CF₃OCHFClCFClOCF₃.¹² This would suggest a common intermediate. Thus a possible route to these products may be as follows.



Although the major product in the dechlorination reaction, where a mixture of $(\text{CF}_3\text{O})_2\text{CClCF}_2\text{Cl}$ and $\text{CF}_3\text{OCFC1CFC1OCF}_3$ is reacted with zinc, is $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$ (PVM), the presence of compound I indicates that the 1,1 adduct is also losing a trifluoromethoxy group.



Since PVM is the major product obtained in this mixed dechlorination, this loss of methoxide probably occurs to only a minor extent. The quantities and relative proportions of the decomposition products recovered would indicate that compounds II and III are decomposing further. This is substantiated to some extent, in that CO_2 is invariably present as a product of this reaction.

C. Reactions of $\text{CF}_3\text{SOCH}_2\text{CF}_3$

The ease with which trifluoromethanesulfenyl chloride reacts with an alcohol to form a thioperoxide linkage¹³ suggested the possibility of preparing a polymer having an unusual heteroatomic backbone.

For example, reaction of a disulfenyl chloride with a diol would give a polymer having the following structure.



Since the glass transition temperature of poly-(thiocarbonyl fluoride) is reported¹⁴ to be -118 , the T_g of this poly-(thioperoxide) would probably also be quite low.

In anticipation of some of the problems which might arise in the preparation of this polymer, the hydrolytic stability of $\text{CF}_3\text{SOCH}_2\text{CF}_3$ was determined qualitatively by sealing the compound in a glass ampoule in contact with H_2O and with 10% NaOH. These experiments indicate that no hydrolysis occurs on contact with water over a period of months, and little or no reaction occurs on contact with 10% NaOH for the same period of time.

(13) S. Andreades, U. S. Patent 3,081,350, March 12, 1963.

(14) V. Engelhardt, Chem. and Eng. News, **43** (41), 80 (1965).

Past experience has shown the difficulty in obtaining pure $\text{ClSCF}_2\text{CF}_2\text{SCl}$. In order to determine whether an exchange type of reaction may be used in the polymer forming reaction, $\text{CF}_3\text{SOCH}_2\text{CF}_3$ was reacted with CH_3OH .

On addition of the alcohol to the thioperoxide an immediate exotherm was noted and a low boiling product was collected. GLC analysis indicated mainly one product, but NMR analysis shows a peak at -30.7 ppm ($\text{CF}_2\text{ClCFCl}_2$) which is attributable to CF on S, but also shows other types of hydrogen. Additional work will be necessary to clarify this reaction.

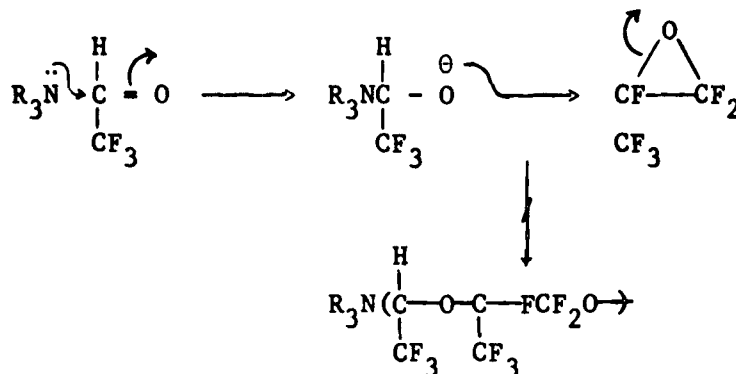
D. Reaction of CF_3CHO with $\text{CF}_3\text{CFCF}_2\text{O}$ and with $\text{C}_2\text{F}_5\text{COF}$

In an attempt to determine the possibility of modifying the intractable nature of poly(trifluoroacetaldehyde), an attempt was made to copolymerize CF_3CHO with $\text{CF}_3\text{CFCF}_2\text{O}$.

Reaction of equimolar amounts of the aldehyde and epoxide in the presence of an anionic catalyst, Et_3N , by simply warming the reactants to room temperature in a sealed tube, gave very little polymer. (Insufficient for characterization.) On opening the reaction ampoule to the vacuum system, the vapor pressure of the liquid present was considerably less than that of either reactant. An infrared spectrum of this product gave no evidence of either the aldehyde or epoxide and showed an absorption maximum at 5.49 microns (Figure 7). This product was identified by NMR analysis as the ester, $\text{C}_2\text{F}_5\text{COOCHFCF}_3$. This is a new reaction which yields a previously unknown ester. Infrared spectra of additional esters are shown in Figures 8-11.

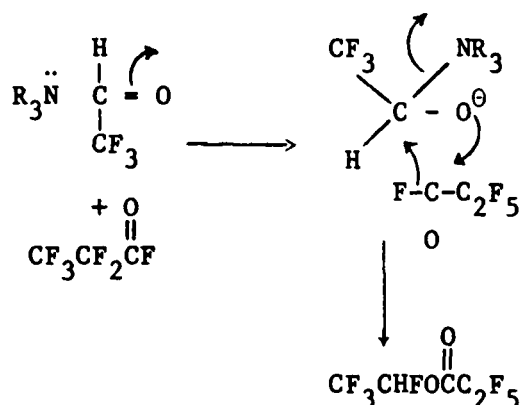
In similar reactions where CF_3CHO and $\text{CF}_3\text{CFCF}_2\text{O}$ were sealed in separate ampoules containing Et_3N , the aldehyde polymerized immediately on warming to give what appears to be a mixture of the trimeric product, $(\text{CF}_3\text{CHO})_3$, and the linear polymer. It is interesting to note that the trimer hydrolyses, on exposure to atmospheric moisture, to give the hydrate $\text{CF}_3\text{CH}(\text{OH})_2$. The epoxide did not polymerize, but an infrared spectrum of the reaction product showed that the epoxide was quantitatively rearranged to the isomeric acid fluoride $\text{C}_2\text{F}_5\text{COF}$.

It is apparent that the amine acts as an initiator with both the aldehyde and the epoxide, but the intermediate anions do not co-react to yield polymeric products.



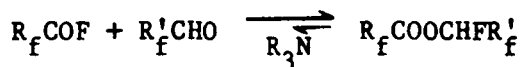
The ease with which the aldehyde polymerizes and the fact that the epoxide rearranges without polymerization would suggest an extremely unstable propoxide ion which rearranges before dimerization or copolymerization can occur.

A possible mechanism for the observed ester formation may be as follows:



This sequence assumes an initial rearrangement of the epoxide to the acid fluoride. A separate reaction was run to show that the acid fluoride will react with the aldehyde. A mixture of an excess of the $\text{C}_2\text{F}_5\text{COF}$ gave the identical product as that obtained with the epoxide.

It was found in the preparation and purification of the esters shown in Table VI that these esters are hydrolytically unstable. Hydrolysis occurs exothermically when they are contacted with water at room temperature. The addition of the acid fluoride to the aldehyde was found to be reversible in the presence of the base used to catalyze the addition. Thus,



At room temperature this equilibrium apparently lies far to the right since good yields of ester are obtainable.

Attempts to distill $\text{C}_3\text{F}_7\text{COOCHFCF}_3$ in the presence of a catalytic amount of Et_3N resulted in complete decomposition to $\text{C}_3\text{F}_7\text{COF}$ and CF_3CHO . On recombination of the reactants in the presence of Et_3N at room temperature, the ester again formed. This ester was successfully distilled, at 72° , after removal of the Et_3N through reaction with gaseous HCl .

E. Preparation of CF_2ClCHO and CF_3CHO

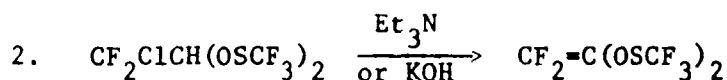
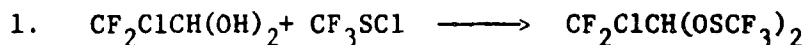
Earlier attempts to prepare polyesters containing the hydrate of trifluoroacetaldehyde as the diol resulted in little, if any, high polymer formation. Since the hydrate, as purchased, contains a considerable amount of water, ethanol, and ethyl hemiacetal, it is believed that part of our difficulty may be attributed to the presence of small amounts of these impurities. As a means of avoiding this problem, it was considered advisable to prepare the aldehyde hydrates in our laboratory.

A high yield of $\text{CF}_3\text{CH}(\text{OH})_2$ and $\text{CF}_2\text{ClCH}(\text{OH})_2$ was obtained by reduction of the corresponding methyl acetate with LiAlH_4 . As found with the commercial products, separation of excess water from the hydrate by distillation is difficult since both hydrates boil at about 105° . The pure aldehyde hydrate is prepared by first dehydrating the crude hydrate, using either P_2O_5 or concentrated H_2SO_4 , and then adding the stoichiometric amount of water to the pure aldehyde. An infrared spectrum of CF_2ClCHO is shown in Figure 12.

Preparation of pure $\text{CF}_3\text{CH}(\text{OH})_2$ is necessary for our polyester studies while the preparation of $\text{CF}_2\text{ClCH}(\text{OH})_2$ was carried out as the first step in the attempted synthesis of $\text{CF}_2=\text{C}(\text{OSCF}_3)_2$ and $\text{C}_2\text{F}_5\text{COOCF}=\text{CF}_2$.

F. Attempted Synthesis of $\text{CF}_2=\text{C}(\text{OSCF}_3)_2$

The following reaction sequence is proposed for the synthesis of this new monomer.



By analogy to the reactions of CF_3SCl with ROH to form the thioperoxides and to the diacylation of the aldehyde hydrates, it would seem reasonable to expect the first step in this reaction to proceed without difficulty. When this reaction was run in an autoclave at 50 to 100° in the presence of pyridine, as an acid acceptor, the pressure in the reactor increased with time. The room temperature pressure rose from zero to 100 psig. Surprisingly, this pressure was found to be due to gaseous HCl in spite of the presence of sufficient pyridine to react with the HCl evolved.

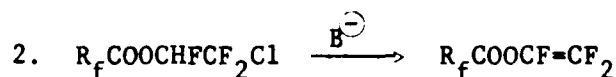
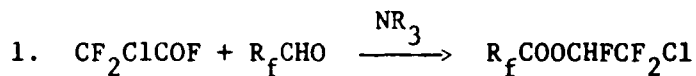
A low yield of an amber liquid was obtained which was difficult to separate on a spinning band distillation column. Infrared spectra of two cuts having boiling ranges of $57-60^\circ$ and $72-94^\circ$ both show C-H stretching

absorption at about 3.38 microns. The lower boiling mixture showed a broad absorption maximum at about 3 microns indicating the presence of a hydroxyl group. This would suggest that both the mono and dithio peroxides are present in the reaction mixture.

Additional work will be necessary to further elucidate this reaction.

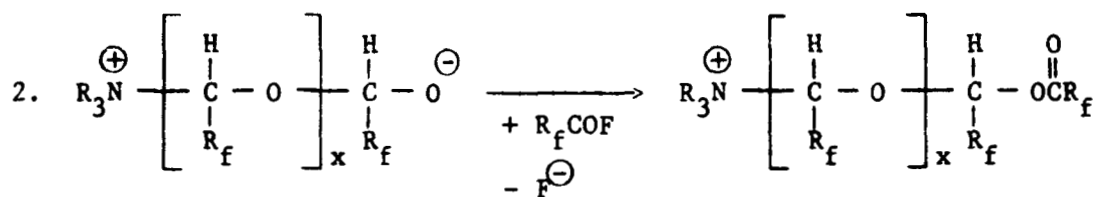
G. Attempted Synthesis of $C_2F_5COOCF=CF_2$

The generality of the acid fluoride-aldehyde reaction was extended to include the addition of perfluoropropionyl fluoride to chlorodifluoroacetaldehyde. The preparation of this new ester presents the possibility of preparing a series of new fluorocarbon vinyl esters. Thus,

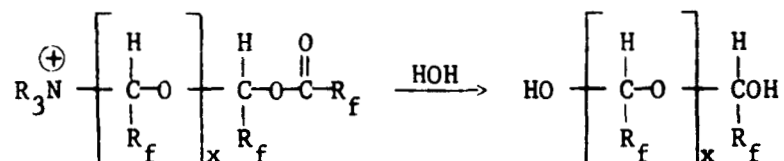


In the first step of this reaction, unlike that of the addition of C_2F_5COF to CF_3CHO , a fair amount of polymer was also obtained along with the ester. ³Polymers of these aldehydes are generally insoluble, infusible solids. The polymer obtained in this reaction was first observed as a viscous solution, but on subsequent exposure to the atmosphere the polymer precipitated. Precipitation is presumed to be due to hydrolysis of the ester. After washing and drying the polymer, it was found to be fusible. The polymer solubility and fusibility indicate a lower molecular weight than normally obtained with these polymers. Since polymerization was carried out in the presence of an acid fluoride, it is possible that termination may be occurring through an acylation step, Step 2.

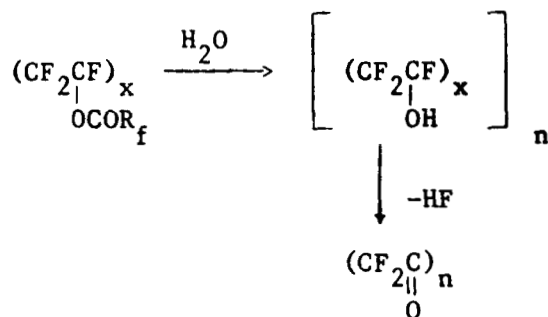




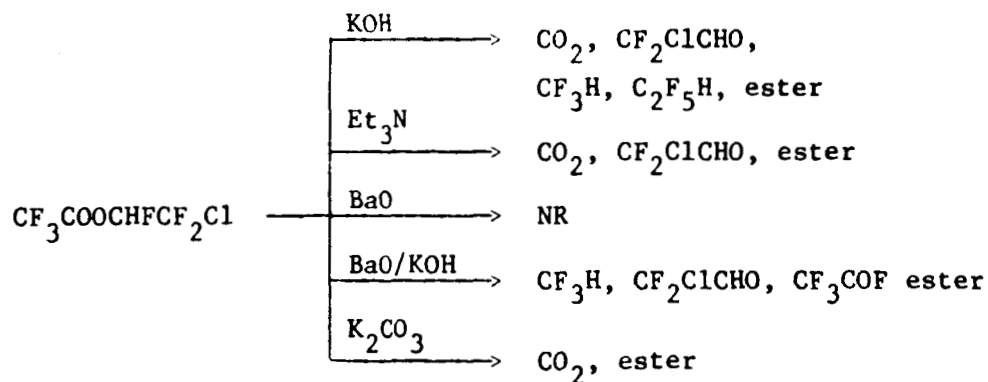
If termination is occurring in this manner, then subsequent hydrolysis should yield a diol which may be used in the preparation of some useful polyurethanes or polyesters. Thus,



Homopolymers and copolymers of these vinyl esters should exhibit good low temperature properties, but ease of hydrolysis may limit their usefulness. However, hydrolysis of the polymer should in itself yield an interesting polyketone. Thus,

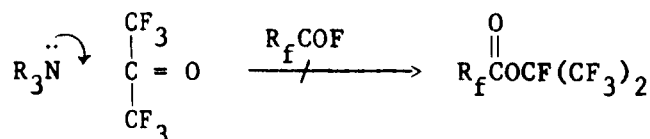


Attempts to dehydrochlorinate $CF_3COOCHFCF_2Cl$, using a variety of reagents has generally resulted in decomposition of the ester. A summary of the reactions attempted are shown as follows.



The products are those identified by infrared analysis. Other product or products were present in some instances which suggested some dehydrochlorination had occurred. An infrared spectrum of the reaction products from the reaction of the ester with KOH showed absorption maxima at 5.48 and 5.61 microns. These maxima would be consistent with that of a perfluorovinyl ester.

The ease with which the base catalyzed addition of the aldehyde to an acid fluoride occurs suggested the possibility of initiating a reaction of an acid fluoride with hexafluoroacetone.



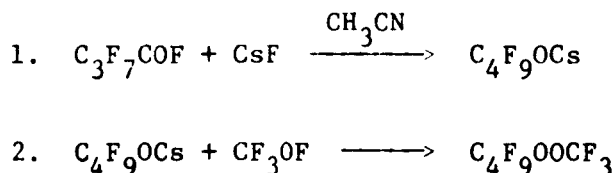
No ester was detected.

H. Attempted Preparation of $\text{C}_4\text{F}_9\text{OOCF}_3$

It is a well established fact that inclusion of heteroatoms in a polymer backbone will lower the glass transition temperature.¹⁵ This is particularly true for highly fluorinated polymers in which no hydrogen bonding is possible.

With this in mind, the fluorination of SOF_2 in the presence of CsF ¹⁶ and the ease with which the fluorocarbon alkoxides may be prepared¹⁷ suggested the possibility of preparing a poly(fluorocarbon peroxide). Based on the good thermal stability of bis(trifluoromethyl) peroxide, $(\text{CF}_3\text{O})_2$, and the highly flexible peroxidic linkage, a polymer of this nature should have good low temperature properties.

Some preliminary experiments have been initiated in an attempt to determine the feasibility of these reactions.

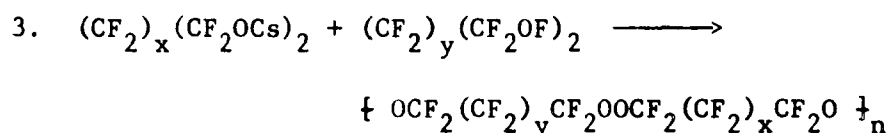
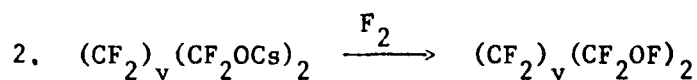
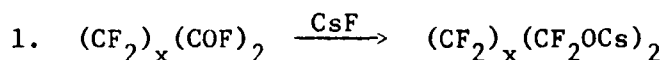


(15) Third Annual Summary Report references.

(16) J. K. Ruff and Max Lustig, J. Inorg. Chem., **3** (10), 1422 (1964).

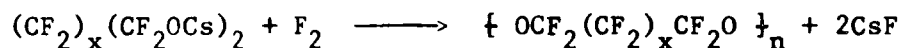
(17) D. C. Bradley, M. E. Redwood, and C. J. Willis, Proc. Chem. Soc., 416 (1964).

The preceding two reactions have been carried out on a small scale and a trace amount of material has been isolated which elutes from a GLC column later than the two starting materials. An infrared spectrum shows no maxima below 7.43 microns. Should this product prove to be the desired peroxide, then the following reaction sequence may be used to prepare a polyperoxide.



Where x and y are zero the polymer would be equivalent to that obtained by Caglioti¹⁸ from the γ -ray induced copolymerization of O_2 and C_2F_4 .

A simpler one-step polymerization may be carried out by reacting a stoichiometric amount of F_2 with the dialkoxide, as shown.



I. Synthesis of $(\text{CF}_3)_2\text{CFCO}(\text{CF}_2)_3\text{COCF}(\text{CF}_3)_2$

Krespan¹⁹ and Engelhardt²⁰ have shown that fluorocarbon ketones will copolymerize, under free radical conditions, to give polymers containing oxygen in the polymer chain. This unusual reactivity of fluorocarbon ketones and the tendency for 1,6 dienes to undergo cyclopolymerization^{21,22} suggested the possibility of preparing an unusual fluorocarbon polyether.

(18) V. Caglioti, A. Delle Site, M. Lenzi, and A. Mele, J. Chem. Soc., 5430 (1964).

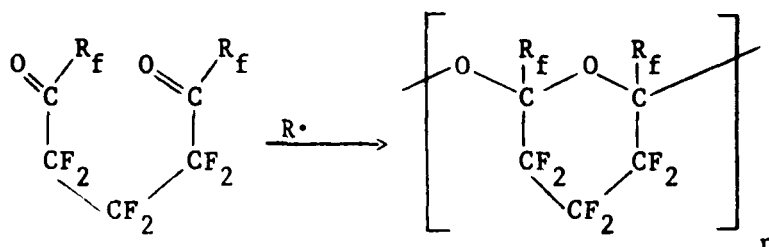
(19) C. Krespan, Seminar at the University of Florida, 5 Feb. 1965.

(20) V. A. Engelhardt, 3rd International Symposium on Fluorine Chemistry, Munich, Germany; also Chem. and Eng. News, **43**, (41), 80 (1965).

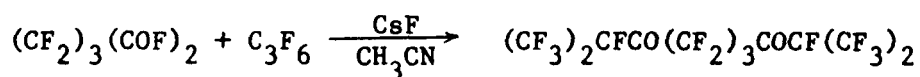
(21) G. Butler and R. Angelo, J. Am. Chem. Soc., **79**, 3128 (1957).

(22) G. Butler, A. Cranshaw, and W. Miller, J. Am. Chem. Soc., **80**, 3615 (1958).

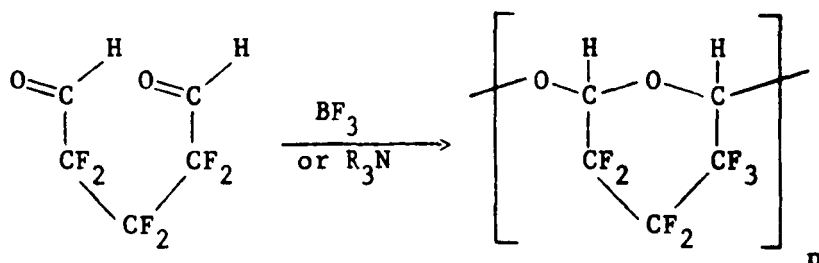
Thus,



A diketone where R_f is a perfluoroisopropyl group was prepared in about 64% yield using the method of Fawcett and Smith.²³ An infrared spectrum of this diketone is shown in Figure 14.



No attempt has yet been made to homopolymerize this diketone. The bulkiness of the isopropyl group would seem to preclude the possibility of forming a cyclo-polymer, but other less hindered 1,5 diketones or unsaturated ketones may be prepared, the simplest being perfluoroglutaraldehyde.



(23) F. S. Fawcett and R. D. Smith, U. S. Patent 3,185,734, May 25, 1965.

EXPERIMENTAL

Chromatographic analyses were run at room temperature on a non-commercial gas chromatograph. The detection system was a thermal conductivity cell and helium was used as the carrier gas. The columns were 3/8" I. D. Pyrex glass, 8' long, packed with HMDS/Chromosorb with 25% ethyl ester of Kel-F acid 8114 as the stationary phase. Exceptions are noted in the text.

Infrared analyses were obtained using a Beckman IR-5.

NMR spectral analyses were carried out at RT using a Varian high-resolution nuclear magnetic resonance spectrometer Model V-4300-2, provided with field homogeneity control, magnetic insulation and super-stabilizer. Chemical shifts were determined by side-bands applied with an audio oscillator for which the frequency is continuously monitored by an electronic counter. Unless otherwise noted, the chemical shifts for fluorine are given with respect to external CF_3COOH , and the chemical shifts for hydrogen are given with respect to external TMS.

A. Polymers

1. Polymerization

a) High pressure polymerization.--In the following system it was possible to prepare several grams of polymer at pressures up to 1300 atm. The pressure is generated by using hydraulic pressure²⁴ to collapse a thin-wall metal tube containing the monomers. Initiation is effected either by a free radical initiator or by a radiation source.

Typically, the monomer is added to an evacuated nickel tube (99.5% Ni, 6" x 3/8", O. D., 0.035" wall) containing initiator, which is sealed at one end by crimping and sealing with soft solder. While maintaining the lower part of the tube at -196° the tube is crimped adjacent to the vacuum tubing connection and with the crimping tool in place, to hold a vacuum seal, the tube is removed from the vacuum system and the upper crimp sealed with soft solder.

The polymerization tube is placed in a water filled high pressure reactor (73 cc capacity), the reactor sealed, and the system pressurized with a hand operated hydraulic pump. When using Co^{60} initiation, the apparatus is disconnected from the pump (a ball check valve prevents loss of pressure) and placed in a vertical position centered about 5 cm. from the Co^{60} source.

(24) Enerpac Model 82-102, Enerpac Systems, Butler, Wis.

At termination of polymerization, the polymerization tube is removed from the reactor, cooled with liquid N, and a saw cut made in the tubing to remove unpolymerized monomer. While still at -196° , the polymerization tube is placed in a tube attached to the vacuum system, the system evacuated, and the amount of residual monomer determined by volume.

Caution should be exercised in attempts to homopolymerize tetrafluoroethylene in the system described above. Polymerization of 2.4 g. of tetrafluoroethylene, using azobisisobutyronitrile as the initiator, resulted in almost a quantitative conversion of the monomer to CF_4 . During the warm-up period the violent reaction and accompanying exotherm caused a pressure surge from 18,000 to an estimated 40,000 psi in the 73-cc water-filled reactor.

Larger quantities of polymer, 10 to 20 g., were prepared in the same reactor through bulk polymerization in a 3 phase system. Typically, the initiator is added to the 73-cc high pressure reactor, the reactor is sealed, evacuated and cooled to -196° . The monomers are condensed into the reactor, followed by the addition of deaired, distilled water containing a trace amount of ammonium perfluorocaprylate. When the water is completely frozen, the reactor is removed from the vacuum system and connected to the high pressure hydraulic system. The reactor is warmed to 60° while maintaining a pressure of 10,000 psi. Homogeneous copolymers were obtained in this way. The polymers prepared by these methods are summarized in Table II.

b) Co^{60} initiated polymerization.--Monomer proportions were measured volumetrically on a calibrated vacuum system, condensed into a 13-ml. capacity Pyrex Carius tube, and sealed under vacuum. The reaction tubes, while still frozen, were placed in a sample holder containing six copper tubes concentrically spaced 1.91 cm. from the center of a central 1.78-cm. tube. The samples and sample holder were warmed to room temperature or to -78° , then placed in the radiation chamber, and the Co^{60} capsule lowered into the central tube. The radiation flux was approximately 7×10^5 r/hr. Typical radiation periods were 24 hours. Irradiation of these monomers was carried out at the University of Florida, Gainesville, Florida, through the assistance of Dr. R. J. Hanrahan of the Department of Chemistry. Polymers prepared in this manner are summarized in Table III.

2. Thermal Analyses

In Table IV are shown the results of thermal analyses of MVE, PVE, and BVE copolymers. These analyses were carried out using a Perkin-Elmer Differential Scanning Calorimeter DSC-113. The homopolymer of poly(vinylidene fluoride) was used as a reference.

3. Physical Properties

In Table V are shown the tensile strength and elongation of MVE/ VF_2 and BVE/ VF_2 copolymers at temperatures above and below T_g . Figures 1, 2, 3, and 4 were derived from these data.

TABLE II
Polymers^a

Exp.	Monomer (mM) ^b	Pressure Atm.	Time, hrs. at P (60°)	% Conv.	Pol. Compn. ^c Mole % Ether	Polymer Character ^d
46P	PVE(1.7)/VF ₂ (5.76)	720-1000	23.5	60	18 ^f	Tough elastomer
47P	PVE(2.3)/VF ₂ (4.6)	720-1000	23.5	50	23.3 ^f	Tough elastomer
48P	EVE(1.15)/VF ₂ (2.3)	600-1000	17	1.42 g. polymer	19.5	Tough elastomer [η], 1.00
49P	EVE(0.85)/VF ₂ (2.58)	600-1000	17	1.36 g. polymer	Top 12.0 Bottom 14.7	Tough elastomer [η], 1.55
50P	EVE(0.69)/VF ₂ (2.76)	600-1000	17	1.5 g. polymer	12.6	[η], 0.63
51P	EVE(0.55)/VF ₂ (2.75)	600-1000	17	1.11 g polymer	10.2	[η], ~1.8
56P	PVE(1.15)/VF ₂ (2.3)	615-1000	18.5	36.3	23.2	Elastomer
57P	PVE(0.85)/VF ₂ (2.58)	615-1000	18.5	51.2	24.0	Tough elastomer ^g
58P	PVE(0.69)/VF ₂ (2.76)	615-1000	18.5	58	16.5	Tough elastomer ^g
59P	PVE(0.55)/VF ₂ (2.75)	615-1000	18.5	78	14.4	Tough elastomer ^g
60P	EVE(40)/VF ₂ (120)	1000	21.5	decomposed carbon		
61P	EVE(40)/VF ₂ (120)	530-680 ^e	19	4.75 g. polymer	16	Tough, clear elastomer

TABLE II--Continued

Exp.	Monomer (ml) ^b	Pressure Atm.	Time, hrs. at P (60°)	% Conv.	Pol. Compn. ^c Mole % Ether	Polymer Character ^d
64P	EVE(82.7)/VF ₂ (248)	315-680	19	10.1 g. polymer	16	Tough, clear elastomer
63P	BVE(1.5)/CF ₃ NO(1.5)	480-680 (run at 0°)		2.65 g. polymer	some resil- ience, but appears weak	Tg, -1 to -5°
65P	PVE(48.1)/VF ₂ (165)	547-685 ^e	48	9.43 g. polymer	10.6 - 12.7	Tough elastomer
67P	PVM(0.68)/VF ₂ (273)	680-1000	46	42.6%	2.1 - 2.2	Molded at 160°. Tough plastic film, sol. in acetone
68P	PVM(0.48)/VF ₂ (2.88)	680-1000	46	51.3	1.9 - 2.2	Molded at 160°. Tough plastic film, sol. in acetone
69P	PVM(1.12)/VF ₂ (2.24)	680-1000	46	24.4	3.8 - 4.4	Molded at 160°. Tough plastic film, sol. in acetone. Tg -55 to -57°
70P	MVE(55.0)/VF ₂ (165)	308-685 ^e	21	3.57 g. polymer	12.3 - 12.9	Tough elastomer molded at 120°
71P	MVE(1.12)/VF ₂ (2.24)	515-1000	17	24.4	18.2 - 19.1	Tough elastomer molded at 120°
72P	MVE(0.84)/VF ₂ (2.52)	515-1000	17	30.2	13.1 - 13.2	Tough elastomer molded at 120°
73P	MVE(0.67)/VF ₂ (2.68)	515-1000	17	31.6	10.1 - 10.7	Tough elastomer molded at 120°

TABLE II--Continued

Exp.	Monomer (mm) ^b	Pressure Atm.	Time, hrs. at P (60°)	% Conv.	Pol. Compn. ^c Mole % Ether	Polymer Character ^d
74P	MVE(0.56)/VF ₂ (2.80)	515-1000	17	--	8.3 - 8.45	Molded at 120° plastic film
75P	MVE(56.4)/VF ₂ (240)	232-685	21	7.48 g. polymer	12.5	Tough elastomer
80P	TO(2.86)/TFE(18.4)	1000	--	0.45 g. polymer	--	Molded to a tough plastic film
81P	EVE(83)/VF ₂ (248) ^e	(Pressure surge exceeded 22,000 psi., carbonization)				
83P	BVE(1.07)/VF ₂ (2.14)	600-1000	--	56	25.1	Molded at 93°. Hazy elastomer
84P	BVE(0.8)/VF ₂ (2.4)	600-1000	--	--	17.2	Hazy elastomer, tougher than 83P
85P	BVE(0.64)/VF ₂ (2.57)	600-1000	--	58	13.6	Molded at 135°. Hazy, tough elastomer
86P	BVE(0.53)/VF ₂ (2.68)	600-1000	--	56	13.4	Molded at 135°. Hazy, tough elastomer
90P	MVE(49.3)/VF ₂ (148) ^e	500	23	84	16.7	Tough elastomer
92P	TO(3.9)/VF ₂ (8.6)	1000	21	--	12.4	Molded to a weak elastomer at 100°
93P	TO(4.2)/VF ₂ (4.3)	1000	66	2.5 g. polymer	--	Elastomer
94P	TO(4.0)/VF ₂ (8.6)	1000	66	2.5 g. polymer	--	Weak elastomer

TABLE II--Continued

Exp.	Monomer (mm) ^b	Pressure Atm.	Time, hrs. at P (60°)	% Conv.	Pol. Compn. ^c Mole % Ether	Polymer Character ^d
95P	TO(4.2)/VF ₂ (13.0)	1000	66	2.1 g. polymer	--	Tacky solid
97P	BVE(50)/VF ₂ (150)	550	17.5	Low	30.3	Weak elastomer
98P	BVE(50)/VF ₂ (150)	500	21	~87	23.06	29.1 Kg/cm ² - 581% elong.
99P	MVE(50.1)/VF ₂ (200)	680	16.75 (80°)	8.6 g. polymer	13.6	224 Kg/cm ² 477% elong.
100P	MVE(50.1)/VF ₂ (250)	680	16.75 (80°)	12 g. polymer	13.0	320 Kg/cm ² , 320% elong.
319	EA(1.7)	(0.07 g. Et ₃ N initiator, R.T., autogeneous pressure)				Waxy solid volatilized on exposure to atm.
320	EA(1.8)/AA91.8)	(0.1 ml. of 0.01% solution of BF ₃ ·Et ₂ O solution)				Waxy solid, volatilizes slowly at R.T.

(a) Vinyl ether copolymers catalyzed with 0.1 to 0.3% azobisisobutyronitrile, 3/8" nickel tube.

(b) MVE, CF₃OCF=CF₂; EVE, C₂F₅OCF=CF₂; PVE, C₃F₇OCF=CF₂; BVE, C₄F₉OCF=CF₂; PVM, (CF₃O)₂C=CF₂;

TO, C₃F₇O[CF(CF₃)CF₂O]₂CF=CF₂; VF₂, CF₂=CH₂; BA, C₃F₇CHO; AA, CF₃CHO.

(c) Determined by elemental analysis.

(d) Intrinsic viscosity [η] determined in MIBK.

(e) Two phase bulk polymerization described in Experimental section.

(f) Polymer compn. determined from plot of mole fraction ether in polymer vs. mole fraction charged.

(g) Polymer appears to evolve HF, glass container became cloudy on standing.

TABLE III
⁶⁰Co Initiated Vinyl Ether Copolymers

Exp. No.	Monomer (mM) ^a	γ Dose Rep.	% Conv. ^b	Pol. Compn. Mole % Ether	Polymer Character
312	MVE(16.7)/VF ₂ (48.6)	3.6(10 ⁶)	83.6	~25	Molded to transparent film at 330°
313	MVE(16.7)/VF ₂ (48.6)	3.6(10 ⁶)	78.7	~25	Molded same as above
314	MVE(16.7)/VF ₂ (48.6)	3.6(10 ⁶)	78.7	~25	Molded same as above
315	MVE(32.4)/VF ₂ (130)	10.3(10 ⁶)	56.0	~20	Molded to transparent film ₂ at 320°. Tensile 251 Kg/cm ² , 238% elong.
316	MVE(32.4)/VF ₂ (130)	10.3(10 ⁶)	67.5	~20	Molded same as above
317	MVE(32.4)/VF ₂ (130)	10.3(10 ⁶)	70.0	~20	Molded same as above
318	MVE(4.0)/VF ₂ (16)	10.3(10 ⁶)	80.0	~20	Molded same as above
288	PVE(5.0)/TFE(20.0)	6.5(10 ⁶)	~88	--	Molded at 330° to tough plastic
290	PVE(8.33)/TFE(16.7)	6.5(10 ⁶)	~77	--	Molded same as above
308	EVE(1.38)/TFE(4.15)	6.5(10 ⁶)	85	--	Molded same as above
309-11	EVE(64)/TFE(199)	24(10 ⁶)	78	--	Molded at 300° translucent film, similar to PTFE

(a) MVE, CF₃OCF=CF₂; VF₂, CH₂=CF₂; EVE, C₂F₅OCF=CF₂; PVE, C₃F₇OCF=CF₂, TFE, CF₂=CF₂.

(b) Samples 312-318 run initially at -78°, warmed to R.T. during irradiation. 312-318 located 1.91 cm. from Co⁶⁰ source (7 x 10⁵ r/hr.) 315-318 distance not determined.

TABLE IV

Glass Temperature of Vinyl Ether Copolymers^a

<u>Copolymer^b</u>	<u>Wt. % VF₂</u>	<u>Tg °C</u>	<u>Av. Tg °C</u>
VF ₂	100	-43, -44, -45	-44 ^c
90P MVE/VF ₂	66	-33, -33	-33
75P MVE/VF ₂	73	-33, -33, -34	-33.3
74P MVE/VF ₂	81	-35, -36, -37, -38, -42, -42	-38.6
73P MVE/VF ₂	77	-35.5, -36	-35.7
72P MVE/VF ₂	82	-35.5, -36	-35.7
71P MVE/VF ₂	63	-34	
59P PVE/VF ₂	59	-28, -31	-29.5
58P PVE/VF ₂	55	-28, -28	-28
56P PVE/VF ₂	44	-24, -24	-24
86P BVE/VF ₂	57	-24, -26, -26, -26	-25.5
85P BVE/VF ₂	56	-28, -29, -29, -30	-29
84P BVE/VF ₂	49	-24, -26	-25
83P BVE/VF ₂	38	-24, -24, -24	-24

(a) Perkin-Elmer Differential Scanning Calorimeter DSC-1B.

(b) VF₂, CF₂=CH₂; MVE, CF₃OCF=CF₂; PVE, C₃F₇OCF=CF₂; BVE, C₄F₉OCF=CF₂

(c) Accepted value from literature references -45°.

TABLE V
Copolymer Physical Properties

Sample	Temp.	Polymer ^a Compn. (Mole %)	Av. Tensile ^c Strength Kg/Cm ²	Average Ultimate ^c Elongation
100P	24°	MVE(13.0)/VF ₂	320(3,31)	442(3,7)
100P	2°	"	431(2,0)	408(2,1)
100P	-72°	"	626(3,32)	19(3,2)
99P	22°	MVE(13.6)/VF ₂	224(3,16)	477(3,11)
99P	2°	"	323(4,18)	429(4,5)
99P	-72°	"	564(2,25)	20(2,2)
90P	22°	MVE(16.7)/VF ₂ ^b	85(3,4)	502(3,22)
90P	0°	"	142(4,17)	449(4,9)
90P	-20°	"	213(2,1)	350(2,2)
90P	-50°	"	353(4,88)	177(4,44)
90P	-78°	"	495(2,3)	32(2,8)
98P	18°	BVE(23)/VF ₂	29.1(7,2,5)	581(7,62)
98P	2°	"	43,6(4,4)	453(4,15)
98P	-20°	"	161(4,23)	343(4,16)
98P	-50°	"	246(4,40)	129(4,22)
98P	-72°	"	389(2,46)	33,5(2,0)
315-18P	25°	MVE(≈20)/TFE	251(4,26)	238(4,16)
315-18P	-72°	"	462(4,49)	13,2(4,6)

(a) MVE, CF₃OCF=CF₂; BVE, C₄F₉OCF=CF₂; VF₂, CF₂=CH₂; TFE, C₂F₄.

(b) Repeat test, sample molded at 135-140°. (Film used for data shown in Quarterly Report No. 11 was molded at 120°.)

(c) Numbers in parentheses show the number of tests and the average deviation in the test results.

The tensile strength and elongation was determined by suspending a thin film of the polymer sample (about 0.015" thick) in the form of a ring (1.000" I.D. x 1.092" O.D.) between two arbors 5/32" in diameter.

In operation a low stress is placed on the sample (about 1.8×10^{-3} kg/cm²) while at room temperature in order that the ring collapses on the arbors. The sample is then placed in the cryostat, brought to temperature and then a pan is suspended from the lower arbor. The pan is hand loaded with lead shot at specific intervals, and the loading continued until the sample breaks.

B. Acetylation of CF₃CH(OH)₂¹¹

To a 250-ml., 1-neck flask, fitted with a reflux condenser, was added 100 g. (about 0.86 mole) of CF₃CH(OH)₂*, 150 g. (1.47 moles) of (CH₃CO)₂O, and 60 g. of pyridine. After 30² hours at reflux the reaction mixture was washed with H₂O and 10% aqueous NaHCO₃ and dried over Drierite. Distillation on a 35 plate spinning band column gave the following cuts.

Cut No.	Boiling Range	Amount
1	68-110°	4.5 g.
2	114-125°	25.0 g.
3	126-141°	13.0 g.
4	141-151°	4.0 g.
5	151-152°	38.0 g.
	residue	25.0 g.

Refractive index of cut No. 5 was n_D^{20} , 1.3543; lit. ref. for CF₃CH(OCOCH₃)₂ 1.354. GLC analysis, (8' column at 140°, Carbowax as the stationary phase) showed a single peak.

NMR analysis has confirmed the structure assigned to the diacylated hydrate (an infrared spectrum of this compound is shown in Figure 6) and also revealed that cut No. 2 was composed of a 1-to-2 mixture of the monoacylated ethylhemiacetal. The latter product was due to the presence of the hemiacetal in the original reaction mixture. These analyses are given as follows.

* Distilled at 100°, GLC analysis showed four peaks.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
$\text{CF}_3\text{CH}(\text{OH})\overset{\text{O}}{\parallel}\text{CCH}_3 \text{ (I)} \quad \text{CF}_3\text{CH}(\text{OC}_2\text{H}_5)\overset{\text{O}}{\parallel}\text{CCH}_3 \text{ (II)}$				
Fluorine				
A	+4.6	2° x 4.8	2.2	CF ₃ (I)
B	+4.7	2° x 4.1	5.7	CF ₃ (II)
Hydrogen				
A	4.4 tau	4° x 4.1, plus smaller 4°	1.5	CH in I and II
B	6.6	4° x 6.5		CH ₂ in C ₂ H ₅
C	6.85	1°	3.7	OH plus water?
D	8.3	1°	4.5	OOC-CH ₃ , I and II
E	9.2	3° x 6.6	3.0	CH ₃ in C ₂ H ₅ , II



Fluorine	+4.23	2° x 4.4		CF ₃
Hydrogen				
A	3.2 tau	4° x 4.3	0.8	CH
B	8.2	1°	5.0	2CH ₃

C. Reaction of CF₃SOCH₂CF₃ with CH₃OH

To a 50-ml., 1-neck flask, fitted with a reflux condenser was added 4.71 g. (23mM) of CF₃SOCH₂CF₃ and 1.0 g. of CH₃OH. Immediately after addition of the alcohol, GLC analysis showed a third peak having a retention time less than either the thioperoxide or trifluoroethanol. The mixture was refluxed and the volatile product collected in a Dry Ice-acetone cooled trap connected to the condenser. GLC analysis of the low boiling product showed only a single peak, and an infrared spectrum showed four major absorption maxima at 8.38, 9.05, and 13.9 microns. NMR analysis of this product shows a singlet at -30.7 ppm (with respect to CF₂ClCFC1₂) which is attributed to CF₃ on S, but also shows other types of CF₃ and several types of hydrogen.

D. Reaction of $\text{CF}_3\text{CH}(\text{OCOCH}_3)_2$ with $(\text{CH}_2)_4(\text{COOH})_2$

To a 300-ml., 1-neck flask fitted with a heated, packed distillation column was added 35 g. (175 mM) of $\text{CF}_3\text{CH}(\text{OCOCH}_3)_2$ and 25.6 g. (175 mM) of $(\text{CH}_2)_4(\text{COOH})_2$. The reaction mixture was heated to reflux and acetic acid removed as formed. Exchange occurred very slowly and after several hours only a trace amount of acetic acid was collected. After refluxing overnight, the reaction mixture became black and only 5 g. of acetic acid was collected before the temperature rose above 118° . The black solid was washed with Et_2O and the ether extract evaporated, leaving a small amount of tar. About 5 g. of adipic acid was recovered.

An infrared spectrum of the tar showed C-H stretching absorption at 3.4 microns, C=O stretching at 5.85 microns, and a maxima between 7 and 9 microns not corresponding to that of adipic acid.

E. Reaction of $\text{CF}_3\text{CH}(\text{OH})_2$ with $\text{CH}_2(\text{COOEt})_2$

To a 100-ml., round bottom flask was added 25 g. of $\text{CF}_3\text{CH}(\text{OH})_2$ (containing some H_2O) and 30 g. (188 mM) of $\text{CH}_2(\text{COOEt})_2$. The flask was fitted with a heated distillation column and a distillation head. The reaction mixture was heated to reflux, and over a period of several hours 3.3 g. of distillate was collected, b.p. $78-82^\circ$. GLC analysis (6', Porapak Type Q at 183°) of the distillate indicated H_2O , EtOH , and $\text{CF}_3\text{CH}(\text{OH})_2$ to be present. On continued heating, 4.3 g. of distillate was collected between 82 and 103° . Further heating under vacuum yielded a low viscosity liquid. An infrared spectrum of the product indicated the presence of $\text{CH}_2(\text{COOEt})_2$ and $\text{CF}_3\text{CH}(\text{OH})_2$.

F. Attempted Preparation of $\text{CF}_3\text{OC}\equiv\text{CF}$

To a 500-ml., 3-neck flask fitted with a mechanical stirrer, addition funnel, and a Vigreux distillation column was added 60 g. of zinc dust and 250 ml. of dry dioxane.

The zinc was first activated with a few crystals of ZnCl_2 and a trace of gaseous HBr , then about 20 g. of $\text{CF}_3\text{OCCl}_2\text{CFCl}_2$ was added. The reaction mixture was refluxed overnight at a reflux temperature of 50° (b.p. of $\text{CF}_3\text{OCCl}=\text{CFCl}$). Only a trace amount of material was collected in a LOX cooled trap connected to the distillation head. An infrared spectrum of this material showed absorption maxima at 2.25, 7.8, 7.92, 8.19, 8.5, 9.28, 10.49, 12.13, and 13.85 microns.

Essentially the same results were obtained using DMSO as a solvent.

G. Dechlorination of a $\text{CF}_3\text{OCFC1CFC1OCF}_3/$
 $(\text{CF}_3\text{O})_2\text{CC1CF}_2\text{Cl}$ Mixture

To a 250-ml., 3-neck flask fitted with a mechanical stirrer, an addition funnel, and a Friedrichs condenser connected to a LOX cooled trap, was added 66.0 g. of zinc dust and about 125 ml. of DMSO. The zinc was activated with ZnCl_2 and a trace amount of gaseous HBr . The reaction mixture was heated to 50° and 80 g. of $\text{CF}_3\text{OCFC1CFC1OCF}_3/(\text{CF}_3\text{O})_2\text{CC1CF}_2\text{Cl}$ (71/29 mixture) was added slowly. Reaction occurred immediately upon addition and 61.2 g. of reaction product was collected in the LOX cooled trap. GLC analysis of the reaction product showed three major and two minor products. Two of the major products were identified by IR analysis as CO_2 , 43%, and $(\text{CF}_3\text{O})_2\text{C}=\text{CF}_2$ (PVM), 43%. A vapor density MW of the third peak, 11% was determined as 146-147 g./mole, and an infrared spectrum showed absorption maxima at 5.67 and 5.75 microns.

Distillation of the crude reaction product gave the following cuts:

-4 to 10°	12.2 g.	about 75% PVM
11 to 12°	18.3 g.	about 81% PVM
$12^\circ+$	9.8 g.	pot residue

NMR analysis of the 11% peak showed it to be a mixture of three isomeric compounds, $\text{CF}_3\text{OCC1}=\text{CF}_2$ (45%), cis and trans $\text{CF}_3\text{OCF}=\text{CFC1}$ (44%).²⁵ In addition, there was about 11% of an unknown impurity present.

H. Preparation of $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}=\text{CF}_2$

Aqueous NaOH (10%) was added to 50 g. (0.076 mole) of $\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}(\text{CF}_3)\text{COF}$ to a phenolphthalein end point. The salt was dried under vacuum, then placed in a 150-ml., round bottom flask, and the flask was attached to a vacuum system through a trap cooled to -196° . The system was evacuated and the salt was heated with a flame such that a steady evolution of gas was maintained. The pyrolysis yielded 35 g. of product.

Fractionation of the pyrolysis product on a 23 plate spinning band column gave the following cuts:

<u>Cut</u>	<u>Boiling Range $^\circ\text{C}$</u>	<u>Wt. g.</u>
1 and 2	80- 120°	0.8 g.
3	120- 149°	4.7 g.
4 and 5	149- 153°	23.6 g. (Mainly 153°)
pot	$153^\circ+$	<u>2.0 g.</u>
	Total	31.1 g.

(25) NMR Analytical data given in the Third Annual Summary Report, this contract.

GLC analysis of cuts 4 and 5 (6', 20% SE 301 Gas Chrom P at 58°) indicated one major component with only trace amounts of impurities.

Based on the starting acid fluoride, the yield of $C_3F_7O[CF(CF_3)CF_2O]_2CF=CF_2$ is 52%.

An infrared spectrum of this product is shown in Figure 14.

NMR spectral data for this vinyl ether are given below.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
F-A	+3.9	Broad	7.9	$2CF_3 + OCF_2$
B	+5.5	Broad	4.5	$CF_3 + OCF_2$
C	+8.2	Broad	2.1	OCF_2
D	+38.7	Part of fluoro-vinyl	1.1	$=CF_2$
E	+46.2	Part of fluoro-vinyl	1.0	$=CF_2$
F	+52.9	Singlet	2.0	CF_2 next CF_3
G	+59.7	Part of fluoro-vinyl	1.0	$O-CF=$
H	+67.5	3° plus unresolved	2.1	CF

I. Preparation of $CF_3OCF=CF_2$ and $C_4F_9OCF=CF_2$

Similar to the preparation of other perfluoroalkyl vinyl ethers,⁸ the following reaction sequence was carried out in the preparation of $CF_3OCF=CF_2$ and $C_4F_9OCF=CF_2$.

- $R_fCOF + CF_3CFCF_2O \xrightarrow{CsF} R_fCF_2OCF(CF_3)COF$
- $R_fCF_2OCF(CF_3)COF + 2NaOH \longrightarrow R_fCF_2OCF(CF_3)COONa + NaF$
- $R_fCF_2OCF(CF_3)COONa \longrightarrow R_fCF_2OCF=CF_2 + NaF + CO_2$

<u>Step</u>	<u>Product</u>	<u>b.p.</u>	<u>Yield</u>
1.	$\text{CF}_3\text{OCF}(\text{CF}_3)\text{COF}$	$7-8^\circ$	29
2.	$\text{CF}_3\text{OCF}(\text{CF}_3)\text{COONa}$	-	-
3.	$\text{CF}_3\text{OCF}=\text{CF}_2$	-22 to -20°	77*
1.	$\text{C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{COF}$	$76-80^\circ$	15
2.	$\text{C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{CO}_2\text{Na}$	-	-
3.	$\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2$	61°	68*

* Based on acid fluoride from step 1.

NMR data for $\text{C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{COF}$, $\text{CF}_3\text{OCF}(\text{CF}_3)\text{COF}$ and $\text{C}_4\text{F}_9\text{OCF}=\text{CF}_2$ are shown below. NMR data was also obtained for perfluoro(propyl isopropyl ketone) [isomeric with and difficult to separate from $\text{C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{COF}$]. This ketone is a reaction product of $\text{C}_3\text{F}_7\text{COF}$ with an impurity (C_3F_6) present in the perfluoropropylene epoxide.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
A. $\text{C}_4\text{F}_9\text{OCF}(\text{CF}_3)\text{COF}^*$				
Fluorine				
A	-102.1		2.2	COF
CDHI	+0.3, 2.9, 8.0, 10.6		6.1	CF_2 next to O
F	+5.1		9.2	CF_3
G	+6.1		9.2	CF_3 on CF
K	+49.8		13.2	2CF_2
L	+54.0		2.3	CF
M	+55.8		0.8	CF_2 next to C=O
B. $\text{C}_3\text{F}_7\overset{\text{O}}{\parallel}\text{CCF}(\text{CF}_3)_2^*$				
B	-2.6		4.2	$(\text{CF}_3)_2$
E	+4.6		2.0	CF_3
J	+40.6		1.4	CF_2
N	+113		0.4	CF

* Spectrum obtained on a mixture of these two compounds, Peaks were poorly resolved, structural proof not conclusive.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
C. <u>CF₃OCF(CF₃)COF</u>				
A	TFAA- 102.0 ppm	Broad	1.0	COF
B	-19.6	2°x8.7, 2°x2.4	3.1	CF ₃ on O
C	+6.6	2°x5.3, 2°x2.6	3.0	CF ₃ on CF
D	+55.9	Broad	1.0	CF
D. <u>C₄F₉OCF=CF₂</u>				
A	+5.75	3°x9.0, 3°	3.2	CF ₃
B	+9.3	Complex	2.1	CF ₂ O
C	+39.8	2°x67.7, 2°x87.4	1.0	=CF trans to O
D	+47.3	2°x111, 2°x86.5, 3°	1.0	=CF cis to O
E	+50.4	Complex	4.0	2CF ₂
F	+60.6	2°x110, 2°x66.7, 3°	1.0	=CF gem to O

Infrared spectra of compounds A, C, and D are shown in Figures 15, 16, and 17.

J. Synthesis of R_fCOOCHFR_f'

1. Reaction of CF₃CHO with CF₃CFCF₂O

To a 20-ml. Pyrex ampoule was added 0.2 ml. of Et₃N. The ampoule was cooled to -196°, evacuated, and 30 mM each of CF₃CHO and CF₃CFCF₂O were added. The ampoule was sealed, then allowed to warm to room temperature. After several days at room temperature, the ampoule was reopened to the vacuum system and 6.13 g. of liquid having a vapor pressure less than 400 mm. was recovered. The product of this reaction was identified by infrared and NMR analysis as C₂F₅COOCHFCF₃. Purity was estimated to be 80-85%.

As control samples, 102 mM of CF₃CHO and 60 mM of CF₃CFCF₂O were sealed in separate ampoules each containing 0.2 ml. of Et₃N. Immediately on warming the aldehyde polymerized to a white solid. No observable reaction occurred with the epoxide. After several days at room temperature the ampoules were reopened to the vacuum system.

No volatiles were recovered from the aldehyde reaction. The polymer was a waxy solid which sublimed when heated over a flame. On exposure to atmospheric moisture, depolymerization occurred yielding $\text{CF}_3\text{CH}(\text{OH})_2$. Some solid residue remained. This residue is presumed to be the linear polymer, $\{\text{CF}_3\text{CHO}\}_x$ and the hydrolytically unstable polymer, the trimeric product, $(\text{CF}_3\text{CHO})_3$.

An infrared spectrum of the volatiles from the ampoule containing $\text{Et}_3\text{N}/\text{C}_2\text{F}_5\text{CF}_2\text{CF}_2\text{O}$ showed only the rearranged isomeric acid fluoride, $\text{C}_2\text{F}_5\text{COF}$. No epoxide was present.

2. Reaction of $\text{C}_2\text{F}_5\text{COF}$ with CF_3CHO

Similar to the previous reactions, a 20-ml. capacity Pyrex ampoule was charged with 0.1 ml. Et_3N , 20 mM $\text{C}_2\text{F}_5\text{COF}$, and 9.4 mM of CF_3CHO . The ampoule was sealed and allowed to warm to room temperature. On warming there appeared to be a rapid reaction. The ampoule was cooled to -196° and opened to the vacuum system. Trap to trap distillation yielded a product which had a vapor pressure lower than either of the reactants. An infrared spectrum of this product was identical with that of $\text{C}_2\text{F}_5\text{COOCHFCF}_3$.

3. Reaction of $\text{C}_2\text{F}_5\text{COF}$ with CF_2ClCHO

To a Fischer-Porter aerosol compatibility tube fitted with a pressure gauge, was added 0.2 ml. of Et_3N . The tube was cooled to -196° , evacuated, and 224 mM of $\text{C}_2\text{F}_5\text{COF}$ was added. When warmed to room temperature a pressure of 50 psig. was noted. The reactor was again cooled to -196° and 215 mM of CF_2ClCHO was added in three separate portions. After each addition the reactor was warmed to room temperature and shaken. The pressure decreased after each addition of the aldehyde and was zero psig. after the last addition was made.

Distillation gave the following cuts:

<u>Cut</u>	<u>b.p.</u>	<u>g.</u>	<u>Product</u>
1	27.5°	7.3 g.	$\text{C}_2\text{F}_5\text{COF}$
2	74-76°	14.0 g.	ester
3	pot residue	18.0 g.	mixture of polymer and ester

NMR and infrared analysis of the second cut confirms the structure of the addition product as $\text{C}_2\text{F}_5\text{COOCHFCF}_2\text{Cl}$. The results of the NMR analysis are summarized below under (4).

On exposure to the atmosphere the viscous liquid residue formed a heavy precipitate. After washing with H_2O and drying under a vacuum, a pasty product was obtained which volatilizes without melting when heated over a flame.

4. Synthesis of $\text{CF}_3\text{COOCHFCF}_3$,
 $\text{CF}_3\text{COOCHFCF}_2\text{Cl}$, and $\text{C}_3\text{F}_7\text{COOCHFCF}_3$

Into an evacuated 100-ml. Fischer-Porter aerosol compatibility tube containing 0.5 ml. of Et_3N , was added 38 mM of CF_3COF and 19 mM of CF_3CHO . The reaction mixture was warmed to room temperature, mixed, then cooled to -196° , and 19 mM of CF_3COF and 19 mM of CF_3CHO was added. The cycle was repeated, with warming and mixing between each addition, until 172 mM of CF_3COF and 153 mM of CF_3CHO were added. Distillation of the reaction product through an 18-cm., vacuum jacketed distillation column packed with 1/8" stainless steel helices gave 27.5 g., 83.8% yield of $\text{CF}_3\text{COOCHFCF}_3$, b.p. $31-33^\circ$. Chromatographic analysis showed a single peak.

Similarly prepared were $\text{CF}_3\text{COOCHFCF}_2\text{Cl}$, yield 76%; and $\text{C}_3\text{F}_7\text{COOCHFCF}_3$, yield 50%. Initial distillation of the latter compound, attempted in the presence of a trace amount of Et_3N , resulted in total decomposition to $\text{C}_3\text{F}_7\text{COF}$ and CF_3CHO . The ester was distilled without decomposition after addition of gaseous HCl to the reaction mixture.

Infrared spectra of these new esters are shown in Figures 7-11. Confirmative NMR analytical data and elemental analyses are given below and in Table VI, respectively.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
<u>$\text{C}_2\text{F}_5\text{COOCHFCF}_3$</u>				
H	3.88 tau	$2^\circ \times 50$		CHF
F-A-1	7.2 ppm		3.0	CF_3 on CF_2
A-2	7.8	$2^\circ \times 6.0, 2^\circ \times 2.9$	2.9	CF_3 on CHF
B	22.9	4° , very small	2.0	CF_2
C	37.3	$2^\circ \times 50.9, 4^\circ \times 5.7$	1.0	CFH
<u>$\text{C}_2\text{F}_5\text{COOCHFCF}_2\text{Cl}$</u>				
F-A	-5.0	$2^\circ \times 10.5, 2^\circ \times 3.4$	2.1	CF_2Cl
B	+6.6	1°	2.9	CF_3
C	+45.5	1°	1.9	CF_2
D	+68.9	$2^\circ \times 51.2, 3^\circ \times 10.3$	1.0	CFH
H-A	3.92 tau	$2^\circ \times 51.2, 3^\circ \times 3.3$		CFH

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
<u>CF₃COOCHF₂CF₃</u>				
F-A	-0.66	1°	3.0	CF ₃
B	+7.75	2°x6.0, 2°x3.0	3.0	CF ₃
C	+75.0	2°x50.3, 4°x5.7	1.3	CFH
H-A	4.00 tau	2°x50.0, 4°x3.0	-	CFH
<u>CF₃COOCHF₂CF₂Cl</u>				
F-A	-5.11	2°x10.8, 2°x3.4	1.9	CF ₂ Cl
B	-1.00	1°	3.0	CF ₃
C	+68.5	2°x51.6, 3°x10.4	1.3	CFH
H-A	3.84 tau	2°x51.0, 3°x3.0	1.0	CFH
B	5.34	2°x52, 4°	Ca 0.02	CFH
C	6.88	2°x52, 3°x 3	Ca 0.05	CFH
<u>C₃F₇COOCHF₂CF₃</u>				
F-A	+4.61	3°x8.66	3.0	CF ₃
B	+7.43	2°x6.0, 2°x3.0	2.9	CF ₃
C	+43.2	4°x8.9, 3°x1.8	2.2	CF ₂
D	+50.7	3° x 1.5	2.0	CF ₂
E	+75.1	2°x50.3, 4°x6.0	1.3	CFH
H-A	3.90 tau	2°x50.0, 4°x3.0	1.0	CFH
B	8.28	Sharp singlet	Ca 0.15	H ₂ O?

TABLE VI

Elemental Analysis of Fluorocarbon Esters

Compound	b.p.	d ₄ ²⁰	Analysis								Yield	
			Calcd.				Found					
			C	H	Cl	F	C	H	Cl	F		
CF ₃ COOCHCF ₃	31-33°											84
CF ₃ COOCHFCF ₂ Cl	59°	1.507	20.8	0.43	15.4	-	20.8	0.5	15.5	-		76
C ₂ F ₅ COOCHFCF ₂ Cl	76°											53
C ₃ F ₇ COOCHFCF ₃	51-52°	1.529	22.7	0.38		64.8						
C ₃ F ₇ COOCHFCF ₃	72°	1.554	22.9	0.32		66.6	23.0	0.39		66.5		50

K. Preparation of $\text{CF}_2\text{ClCOOCH}_3$

To a 2-liter, 3-neck flask fitted with a reflux condenser, addition funnel, and a mechanical stirrer was added 304 g. (9.5 moles) of CH_3OH and 500 g. of CF_2ClCOOH . While stirring, 133 ml. of concentrated H_2SO_4 was added slowly. The reaction mixture was refluxed for 1.5 hours. Distillation of the reaction product gave 430 g. (78% yield) of $\text{CF}_2\text{ClCOOCH}_3$, b.p. $79-80^\circ$.

L. Reduction of $\text{CF}_2\text{ClCOOCH}_3$

To a 500-ml., 3-neck flask equipped with a nitrogen inlet tube, mechanical stirrer, and a condenser with a drying tube attached, was added 300 ml. of anhydrous Et_2O and (cautiously) 10 g. (264 mM) of LiAlH_4 . The slurry was stirred for 1.5 hours, then refluxed for 45 minutes.

To a second 1-liter, 3-neck flask fitted with a nitrogen inlet tube, a pressure compensated addition funnel, mechanical stirrer, and a condenser, was added a solution of 144.5 g. (1 mole) of $\text{CF}_2\text{ClCOOCH}_3$ in about 1.5 times its volume of dry Et_2O . The flask was cooled in a Dry Ice-acetone bath and, while flushing with nitrogen, the LiAlH_4 slurry was transferred to the addition funnel. While stirring, the LiAlH_4 was added slowly over a period of about 2.5 hours. To the reaction mixture was added 25 ml. of EtOH containing 5% H_2O . After warming to room temperature the reaction mixture was poured onto crushed ice containing 75 ml. of concentrated H_2SO_4 . The ether was stripped through a packed column to a head temperature of 90° , and remaining in the distillation flask was 148 g. of crude $\text{CF}_2\text{ClCH(OH)}_2$.

M. Dehydration of $\text{CF}_2\text{ClCH(OH)}_2$

To a 250-ml., 3-neck flask fitted with an addition funnel, a stirrer, and a gas outlet tube, was added 69 g. (about 0.5 mole) of the crude $\text{CF}_2\text{ClCH(OH)}_2$. While stirring, 50 ml. of concentrated H_2SO_4 was added slowly. Because of the exotherm, the reaction mixture had to be cooled during addition of H_2SO_4 . No dehydration occurred during the acid addition, but on subsequent heating of the reaction mixture, 42 g. (0.367 mole) of CF_2ClCHO was collected in a finger trap (at -78°). Because of the reactivity of this aldehyde, analysis is difficult. An infrared spectrum showed no major impurities. As a further indication of purity, subsequent polymerization gave essentially 100% conversion to polymer. This polymer is a hard, brittle solid.

Similar to CF_3CHO , it is necessary to store this aldehyde under vacuum at -78° to prevent polymerization. An infrared spectrum of this aldehyde is shown in Figure 12.

Regeneration of pure aldehyde hydrate was effected by adding slightly less than the theoretical amount of H_2O to the aldehyde in a sealed ampoule.

N. Attempted Reaction of C_2F_5COF with CF_3COCF_3

To an evacuated Pyrex ampoule was added 0.1 ml. of Et_3N , 57 mM of C_2F_5COF , and 57 mM of CF_3COCF_3 . The ampoule was sealed, and the reaction mixture was warmed to room temperature. When the ampoule was reopened to the vacuum system, 94 mM of low boiling volatiles were recovered, and a small amount of a red high boiling liquid remained in the ampoule.

No apparent reaction occurred. The high boiling liquid obtained is presumed to be an Et_3N -acid fluoride complex noted on other occasions. This would account for the apparent loss of reactants.

O. Attempted Preparation of $CF_2ClCH(OSCF_3)_2$

A 100-ml. autoclave was charged with 22 g. (0.166 mole) of $CF_2ClCH(OH)_2$, 26 g. (0.33 mole) of pyridine, and 41 g. (0.30 mole) of CF_3SCl . When warmed to room temperature, the autoclave showed no pressure. After heating for 19 hours at 50° , the pressure was 100 psig. At this time the temperature was increased to 100° and maintained at this temperature for 24 hours. The pressure increased to 400 psig. When cooled to room temperature, the pressure was 100 psig.

The autoclave was vented through an evacuated trap at -196° . Collected in this trap was gaseous HCl , and remaining in the autoclave were two immiscible high boiling liquids. On standing, the tar-like phase solidified leaving an amber liquid. This liquid, about 20 g., was decanted and distilled on an 18-inch spinning band column which gave only a poor separation. Two broad cuts were taken at $57-60^\circ$ and $72-94^\circ$. An infrared spectrum of the first cut showed a broad maximum at 3.0μ , C-H stretching absorption at 3.38μ , two maxima at 5.53μ and 5.87μ and the usual C-F absorption between 7.5μ and 10.0μ . The spectrum of the broad second cut showed C-H stretching absorption at 3.37μ , a weak absorption at 5.53μ and strong maxima at 7.29 , 7.67 , 8.05 , 8.4 , 8.65 , 9.05 , 9.22 , 9.52 , 10.05 , 11.65 and 13.0μ .

P. Preparation of $C_8F_{17}OCF(CF_3)COF$

A mixture of 43 g. (103 mM) of $C_7F_{15}COF$, 15.2 g. (100 mM) of CsF , and 65 ml. of CH_3CN (dried over P_2O_5) was added to a Fischer-Porter aerosol compatibility tube. The tube was cooled, evacuated, and 32 mM of CF_3CFCF_2O (containing about 10-20 mM of $CF_3CF=CF_2$) was added. The tube was warmed to R.T. and shaken. The addition was repeated until about 100 mM of CF_3CFCF_2O was added. A part of the CH_3CN was removed under vacuum and the reaction product was vacuum distilled, yielding 4 g. of product, b.p. $76-78^\circ/35mm$. GLC analysis ($3/6'' \times 5'$, 5% Carbowax 20M on gas-chrom P at 50°) indicated one major product plus three minor components.

An infrared spectrum of the mixture (Figure 18) shows two carbonyl stretch maxima. These maxima are attributed to the presence of both a fluorocarbon acid fluoride and a fluorocarbon ketone. The ketone is due to the presence of C_3F_6 as an impurity in the starting perfluoropropylene epoxide. An NMR spectrum of the mixture showed the impurity level too great to enable a valid interpretation, NMR spectral data for $CF_3(CF_2)_6COCF(CF_3)_2$ is given below.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
<u>$CF_3(CF_2)_6COCF(CF_3)_2$</u>				
A	-2.78	Multiplet	14.0	$(CF_3)_2$
C	+4.82	$3^\circ \times 9.9$	8.3	CF_3
E	+39.5	Broad	4.5	CF_2CO
F	+44.1	Irregular	16.8	$(CF_2)_4$
G	+49.5	Broad	4.1	CF_2 next to CF_3
I	+113.2	Broad	1.5	CF

Q. Attempted Dehydrochlorination of $C_2F_5COOCHFCF_2Cl$

To an ampoule attached to a calibrated vacuum system was added 10 g. (178 mM) of powdered KOH. The KOH was heated for 0.5 hours under vacuum, cooled to -196° , and then 3 g. (11 mM) of $C_2F_5COOCHFCF_2Cl$ was added. The ampoule was warmed slowly. When warmed to about room temperature, a rapid pressure rise was noted and the KOH became discolored. An infrared spectrum of the crude reaction product indicated the absence of the starting ester and, in addition, showed two new absorption maxima and 5.48μ and 5.61μ . Chromatographic analysis (24', Kel-F ester on HMDS chromosorb at R.T.) of an overgas sample of the crude reaction product showed four peaks having proportionate areas of 65, 25, 3, and 7% (in the order of retention times). The first peak was found, by infrared analysis, to contain CO_2 and CF_3H . The second peak was C_2F_5H . Because of a limited amount of product, the last two peaks could not be isolated.

R. Synthesis of $(CF_3)_2CFCO(CF_2)_3COCF(CF_3)_2$ ²³

To a 100-ml. Fischer-Porter aerosol compatibility tube was added 10 g. (67 mM) of dry CsF and 5 ml. of dry acetonitrile. The reactor was cooled to -196° , evacuated, and 11.1 g (44.2 mM) of $(CF_2)_3(COF)_2$ and 13.2 g. (88.4 mM) of C_3F_6 were added. The reaction mixture was heated for 48 hours at 90° . At the end of this time a trace amount of volatiles were removed under vacuum and the higher boiling reaction product, 15.5 g., was separated from the immiscible acetonitrile by decantation.

Chromatographic analysis (8', 15% Carbowax 20M, 80°) showed only a trace (about 10%) of impurity (64.3% yield). Micro b.p. 142°; (lit. 148-151°) d_4^{20} , 1.7950.

An infrared spectrum of this diketone is shown in Figure 13. NMR spectral data is given below.

<u>Designation</u>	<u>Chemical Shift ppm</u>	<u>Pattern and Splitting cps</u>	<u>Rel. Area</u>	<u>Assignment</u>
$(CF_3)_2CFCO(CF_2)_3COCF(CF_3)_2$				
A	-4.63	Doublet	2.2	CF_3 or OCF_2
B	-2.68	Singlet	3.7	CF_3
C	+37.0	Broad	0.53	CF_2
D	+39.2	Doublet	1.03	CF_2
E	+43.9	Triplet	0.44	CF_2
F	+50.1	Broad	0.41	CF_2
G	+51.9	Broad doublet	0.26	CF_2
H	+54.3	Broad	0.26	CF_2
I	+57.0	Doublet, each a quartet	0.19	CF_2
J	+108.4	Doublet	0.40	CF_2
K	+113.4	Broad	0.89	CF

S. Attempted Preparation of $C_4F_9OOCF_3$

Into an evacuated 100-ml. Fischer-Porter aerosol compatibility tube containing 5 g. (33mM) of CsF and 5 ml. of acetonitrile, was condensed 28 mM of C_3F_7COF . At room temperature two liquid phases were noted. When the reactants were mixed, an exothermic reaction occurred, and the granular CsF appeared to change to a finely divided solid having a paste-like consistency. After the exotherm subsided, the acetonitrile was removed under reduced pressure. The reaction tube was then cooled to -196°, and 16 mM of a gaseous mixture containing about 70 mole percent CF_3OF (also containing CF_4 , $(CF_3O)_2$, COF_2) was added. After standing overnight, the pressure dropped from an initial pressure of 30 to 0 psig. The higher boiling product was enriched by trap-to-trap distillation, and GLC analysis (40', Kel-F ester on HMDS chromosorb) showed one major component having a retention time greater than that of the starting materials.

An infrared spectrum of this peak showed principal maxima at 7.43, 8.05, 8.72, 9.43, 10.6, 11.4, and 13.3 microns.

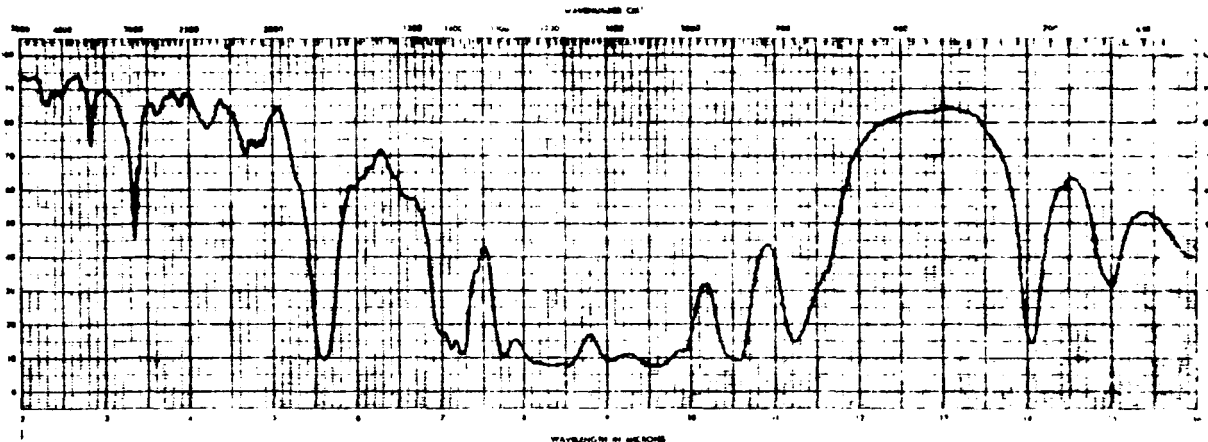


Figure 6. An Infrared Spectrum of $\text{CF}_3\text{CH}(\text{OCOCH}_3)_2$
liquid

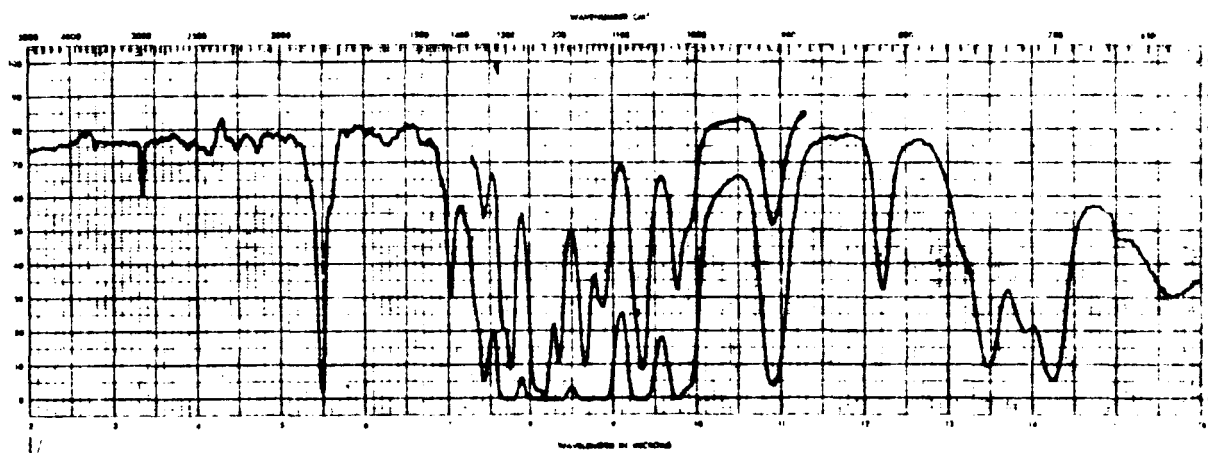


Figure 7. An Infrared Spectrum of $\text{CF}_3\text{CHF}(\text{OCOC}_2\text{F}_5)$
5 mm, 27 mm gas

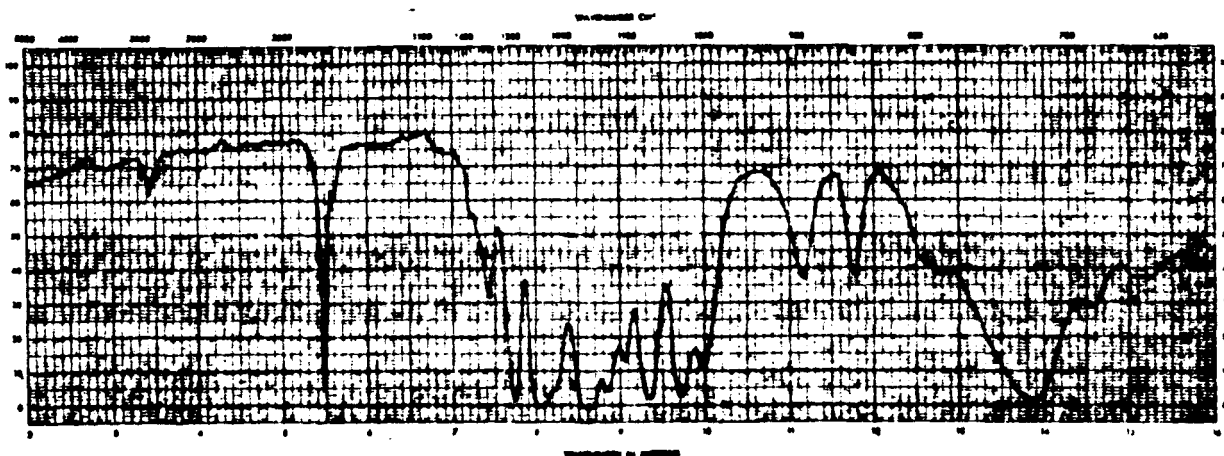


Figure 8. An Infrared Spectrum of $\text{C}_2\text{F}_5\text{COOCHF}_2\text{Cl}$

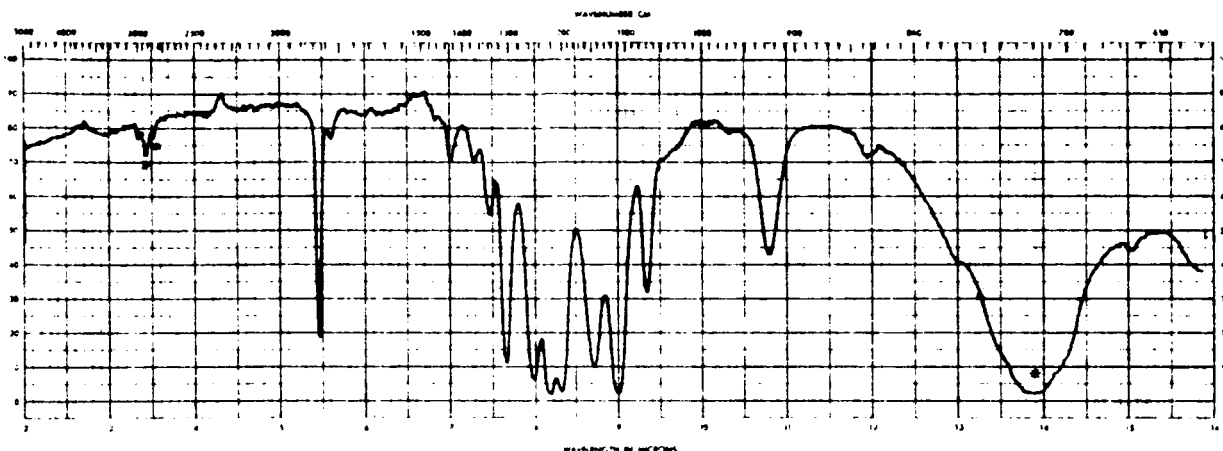


Figure 9. An Infrared Spectrum of $\text{CF}_3\text{COOCHFCF}_3$
30 mm, gas. *Cell

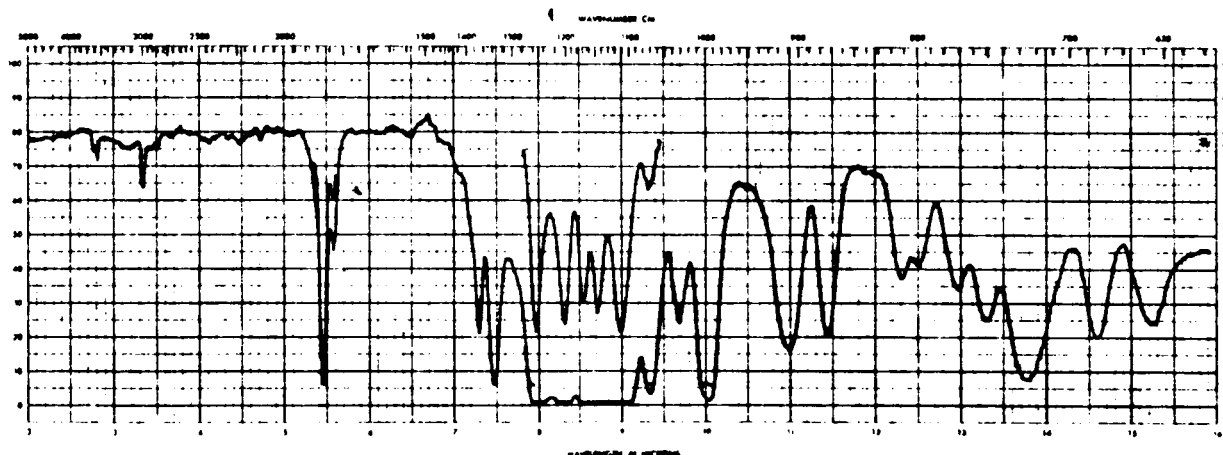


Figure 10. An Infrared Spectrum of $\text{CF}_3\text{COOCHFCF}_2\text{Cl}$
 $p_2 = 10$ mm; 2 and 30 mm

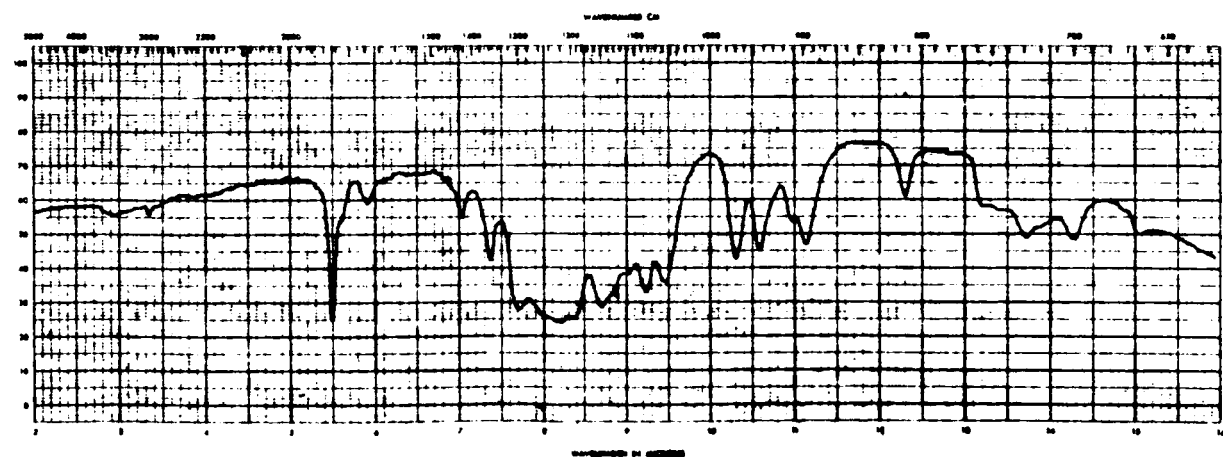


Figure 11. An Infrared Spectrum of $\text{C}_3\text{F}_7\text{COOCHFCF}_3$,
liquid

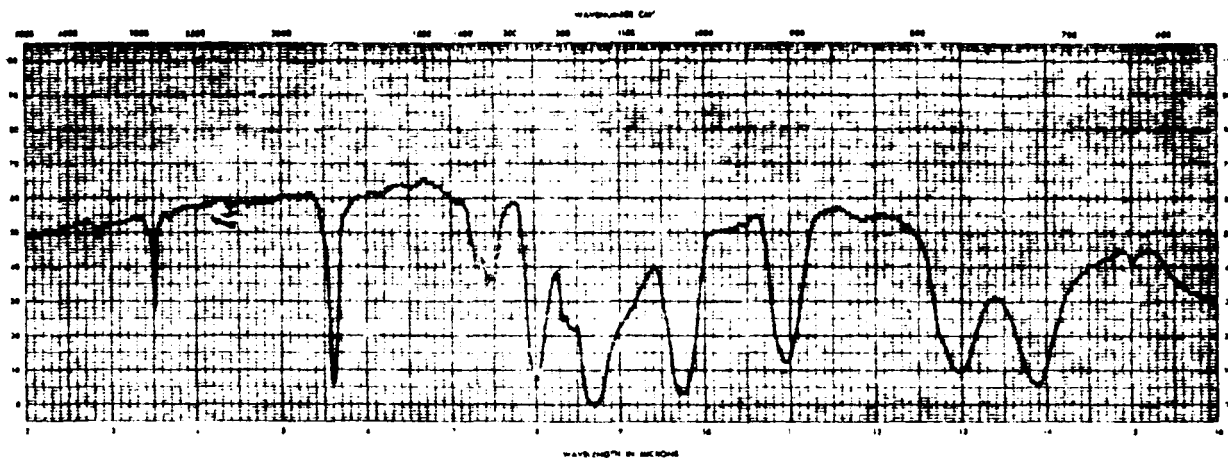


Figure 12. An Infrared Spectrum of CF₂ClCHO

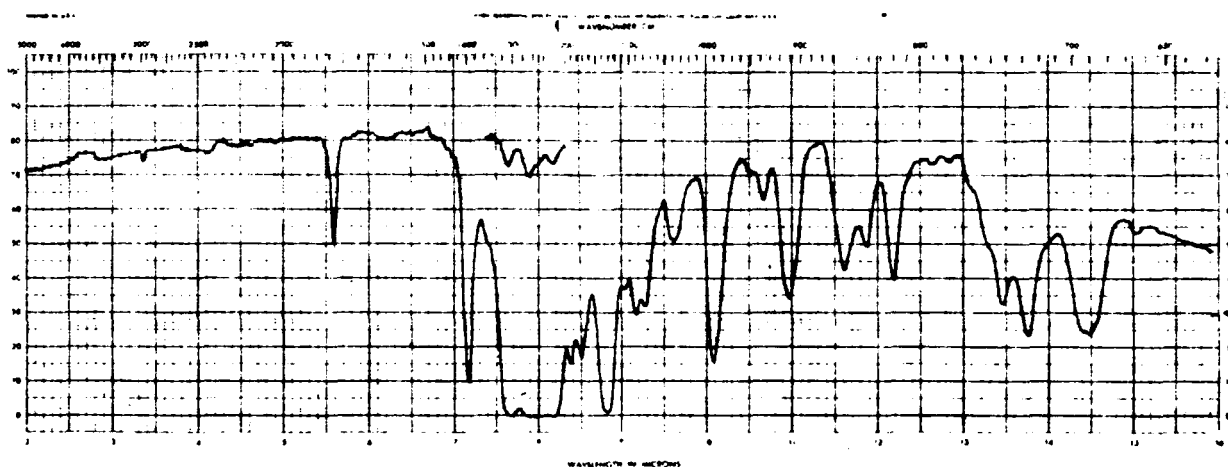


Figure 13. An Infrared Spectrum of (CF₃)₂CFCO(CF₂)₃COCH(CF₃)₂

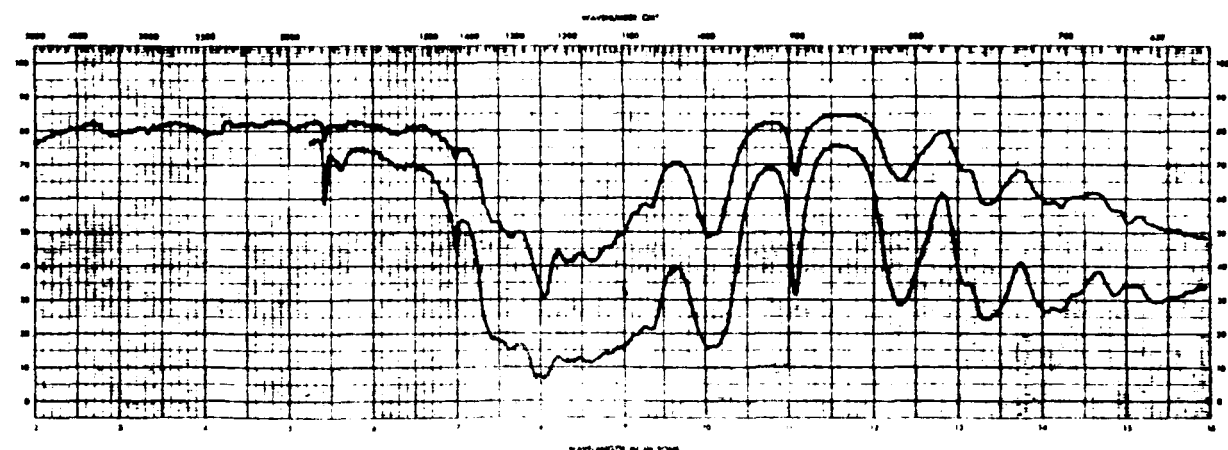


Figure 14. An Infrared Spectrum of C₃F₇O[CF(CF₃)CF₂O]₂CF=CF₂
liquid

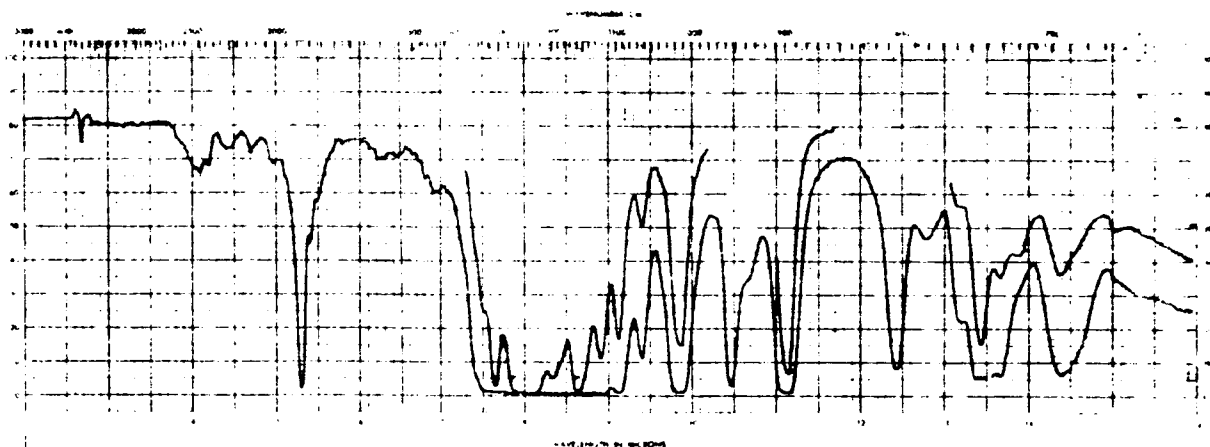


Figure 15. An Infrared Spectrum of $C_4F_9OCF(CF_3)COF$
7 mm, 27 mm gas

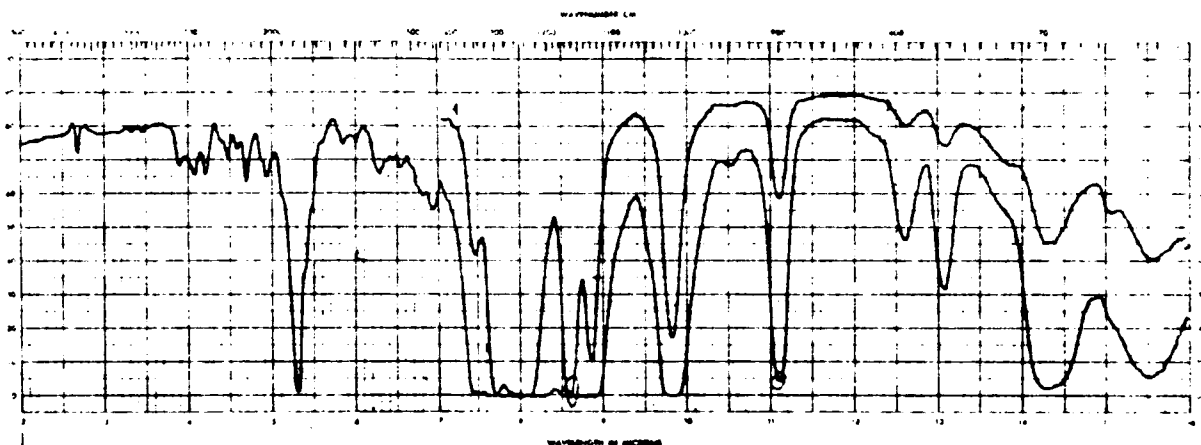


Figure 16. An Infrared Spectrum of $CF_3OCF(CF_3)COF$
5mm, 46 mm gas

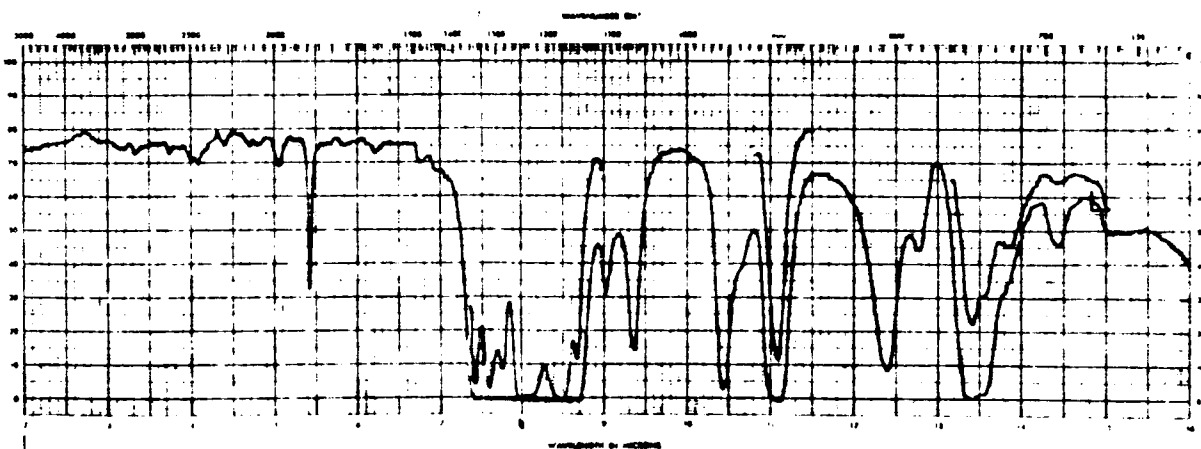


Figure 17. An Infrared Spectrum of $C_4F_9OCF=CF_2$
4 mm, 17 mm gas

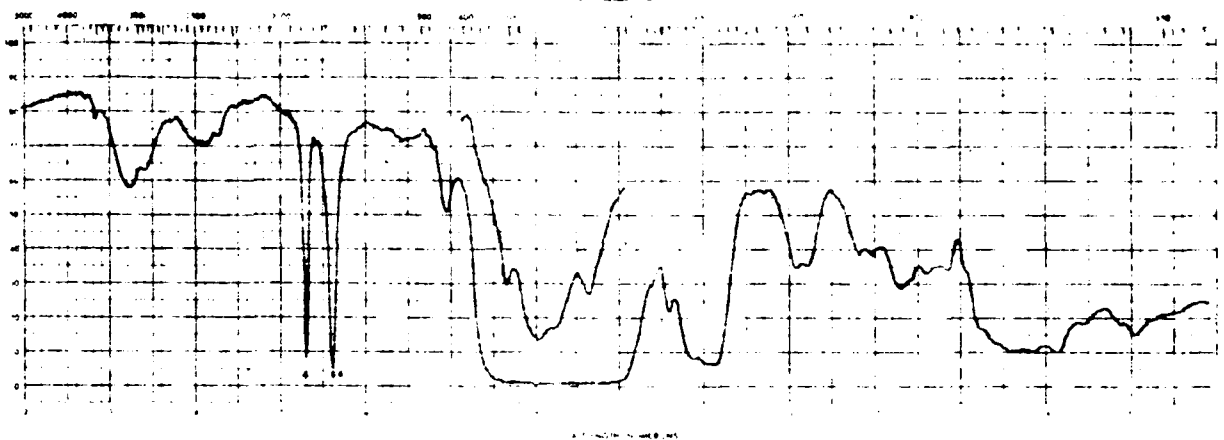


Figure 18. An Infrared Spectrum of a Mixture of
 $\text{C}_8\text{F}_{17}\text{OCF}(\text{CF}_3)\text{COF}$ and $\text{C}_7\text{F}_{15}\text{COCF}(\text{CF}_3)_2$,
 liquid

APPENDIX

ANNOTATED BIBLIOGRAPHY

May, 1966 through January, 1967

INTRODUCTION

This bibliography was prepared from references obtained mainly from Chemical Abstracts but contains, in addition, references taken from a number of primary sources. Major emphasis was placed on references to fluorine-containing monomers and polymers and to thermal properties of all classes of polymers.

In past Annual Summary Reports references covered from 1957 to the date of the report. For the sake of brevity and to eliminate the need for duplicating earlier references, the present bibliography covers only the period of this report - May, 1966 through January, 1967.

As in the past, the great number of references in the categories covered necessitated selecting references which were considered to be of most significance to the present investigation. The choice of references is somewhat subjective, but it is felt that the cross-section given is a useful representation of the literature to date.

The references listed have been categorized with respect to the general subdivisions shown below. Once again for the sake of brevity, no cross-referencing has been done; hence, where a paper was concerned with more than one subdivision the reference, in general, was placed in the category of greatest importance. Copolymers were placed in the earliest listed monomer category with the exception of the vinyl ethers and thioethers, the copolymers of which were included under the main heading of vinyl ethers.

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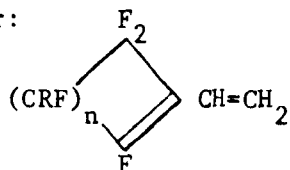
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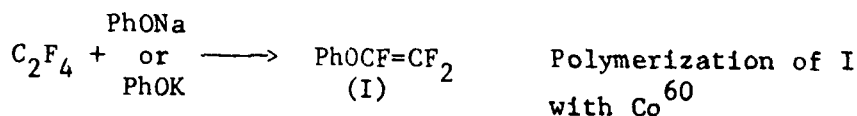


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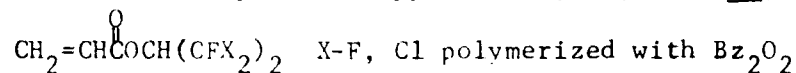


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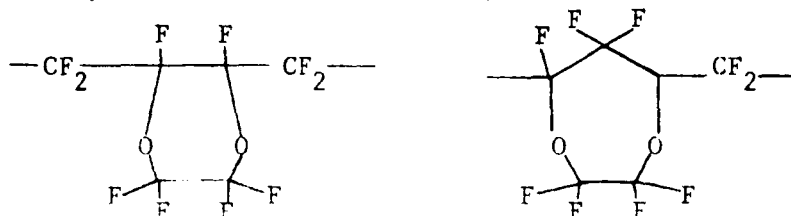
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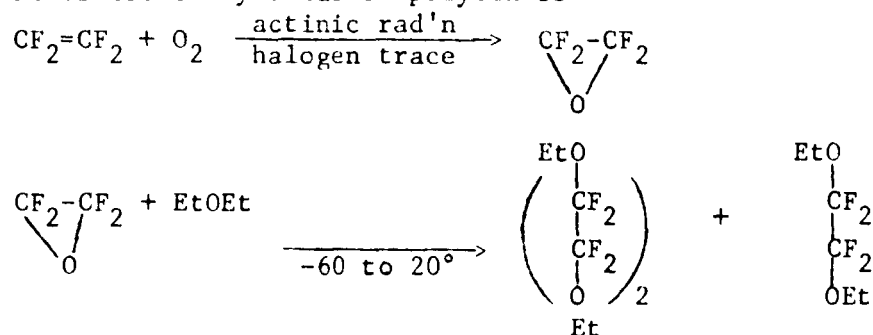
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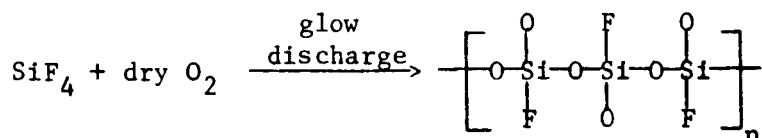
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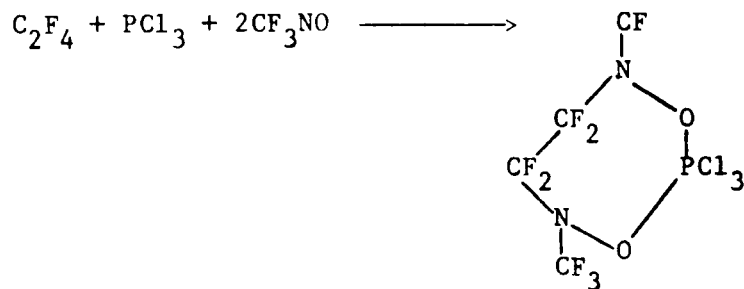
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alkyltriazines). Triazines prepared by cyclodehydration
of perfluorobutyric anhydride and imidoylamidines

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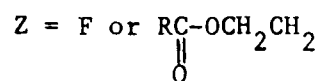
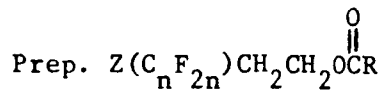
In many radiation induced polymerizations trace amounts
of H_2O retard rate

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Trasick, R. W. (to duPont) U. S. 3,239,557, C.A. 64, 14098c



R = alkyl or alkenyl

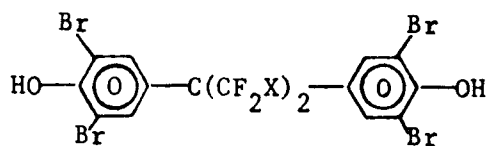
n = 1-16

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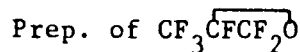
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Prep. of



X = F, Cl

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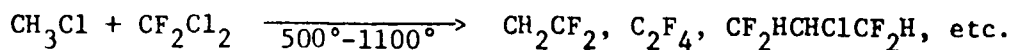
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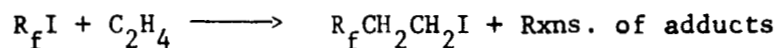
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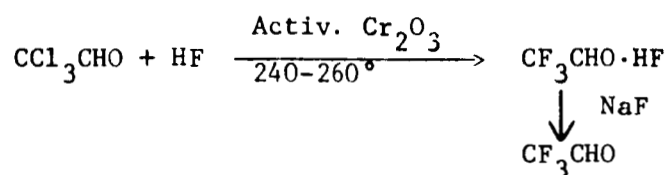
Madai, H., East Ger. 42,730, C.A. 64, 17421b



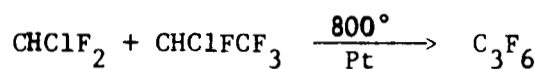
Bloechl, W., Neth. Appl. 6,506,069, C.A. 64, 17421c



duPont, Neth. Appl. 6,508,807, C.A. 64, 17427d

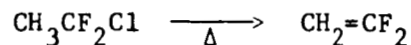


VEB Fluorwerke Dohna., East Ger. 43,244, C.A. 64, 19408h



Miville, M. E., Earley, J. J. (to Pennsalt)

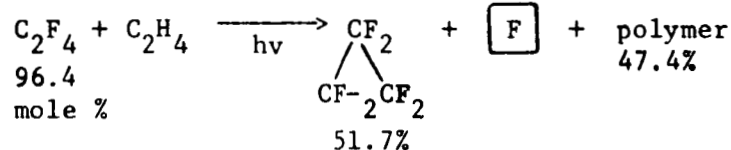
U. S. 3,246,041, C.A. 64, 19410e



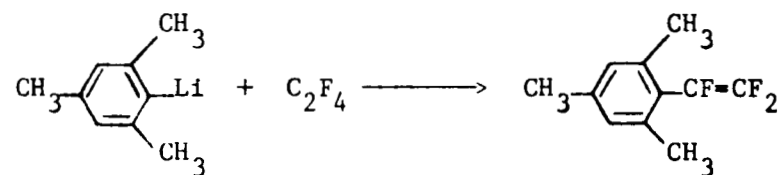
Banks, R. E., Haszeldine, R. N., et al., C.A. 64, 19433a

Isomerization of the dimer of tetrafluoroallene
to perfluoro-2-methyl-3-methylenecyclobutene

Mastrangelo, S.V.R., (to duPont) U. S. 3,228,864



Petrii, O. P., et al., C.A. 64, 19462d



Tedder, J. M., Walton, J. C., C.A. 65, 2107a

Addition of trichloromethyl radicals to fluoroethylenes

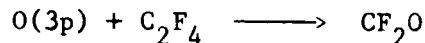
Muramatsu, H., et al., C.A. 65, 3723c

Synthesis of fluorine-containing butadienes

Posta, A., Paleta, O., C.A. 65, 3724h

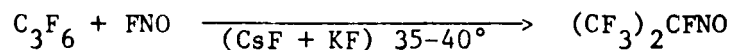
The addition reaction of CCl_4 to CTFE

Saunders, D., Heicklen, J., C.A. 65, 3731d



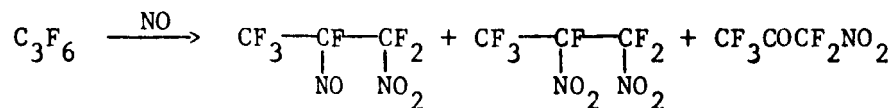
Bloechl, W., Neth. Appl. 6,511,871, C.A. 65, 3907b
Fluoroalkyl chlorosilane monomers

Dyatkin, B. L., et al., C.A. 65, 5320h



Tatlow, J. C., et al., C.A. 65, 5350c
Reductive coupling of perfluorovinylhalides in the presence of copper-bronze

Bagley, E., et al., C.A. 65, 5352h



Daikin Kagyo Co., Ltd., Brit. 1,027,435, C.A. 65, 5366c

Recovery of C_2F_4 and C_3F_6 from CHClF pyrolysis

Pennsalt, Neth. Appl. 6,512,899, C.A. 65, 5366d
Prep. C_2F_4 and C_3F_6 by pyrolysis of HCF_3

Scherer, O., et al., C.A. 65, 5375h
Prep. and rxns. of perhalogenated α, β -unsaturated ketones

Pummer, W. J., Wall, L. A., C.A. 65, 5390f
Pentafluorophenyl alkyl and vinyl ethers

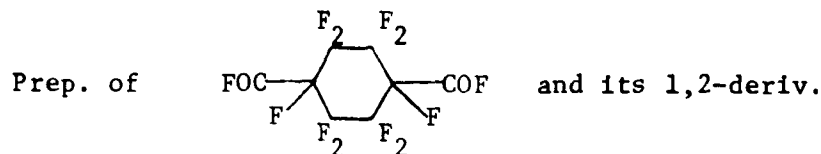
Sianesi, D., et al., C.A. 65, 7004e
The chemistry of hexafluoropropylene epoxide

Janz, G. J., Flannery, J. B., C.A. 65, 7013f
 $\text{CF}_3\text{CN} + \text{CH}_2=\text{CHF} \longrightarrow \text{CF}_3\text{CH}_2\text{CHFCN} + 13\% \text{ higher telomers}$

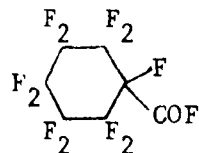
Mueller, R., Dressler, M., East Ger. 43,698, C.A. 65, 7057a

Prep. of CTFE by dechlorination of $\text{CF}_2\text{ClCFCl}_2$

Allied Chem. Corp., Neth. Appl. 6,511,438, C.A. 65, 7076e



Also:



Pittman, A. G., Wasley, W. L., Neth. Appl. 6,512,238, C.A. 65, 7362g

Fluoroesters with ketone group

Cheburokov, Y. A., et al., C.A. 65, 8740f

Perfluorotetramethylallene

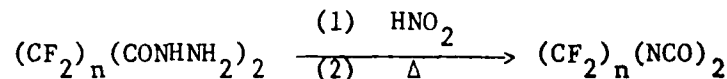
Knunyants, I. L., et al., C.A. 65, 8749b

Nitration of C_3F_6 by NO_2 and a study of the nitration products

Timofeyuk, G. V., et al., C.A. 65, 8947b

Synthesis of para-substituted α, β, β -trifluorostyrenes

Knunyants, I. L., et al., C.A. 65, 10482b



$n = 3, 4$

Salinovich, O., et al., C.A. 65, 11747a

The gas phase fluorination of carbonyl sulfide

Knunyants, I. L., et al., C.A. 65, 12100h

Fluorinated monocarboxylic acids

Dyatkin, B. L., et al., C.A. 65, 12102c

Reactions of nitryl fluoride with alkyl perfluoro-vinyl ethers. Synthesis of α -nitroperfluorocarboxylic acid esters

Sedlak, J. A., Matsuda, K., (to Am. Cy.)

U. S. 3,262,967, C.A. 65, 12112a

α -fluoroacrylates

- Yakubovich, A. Ya., et al., C.A. 65, 12205c
Syntheses in the 1,3,5-triazine series. Esters of iminoperfluorocarboxylic acids; synthesis, properties, mechanism of cyclopolymerization into 1,3,5-triazine derivatives
- Kirk-Othmer Encycl. Chem. Technol., 2nd Ed., C.A. 65, 13534h
Fluorinated carboxylic acids
- Barlow, M. G., et al., C.A. 65, 13523h
Perfluoroalkyl derivatives of nitrogen. Perfluoroalkylnitroso compounds from perfluoroacyl nitrites
- Fritz, C. G., Moore, E. P. (to duPont) U. S. 3,250,807, C.A. 65, 13553h
Dicarboxylic acids of fluorocarbon ethers and fluorides and their esters, amides, and salts
- Moore, E. P., et al. (to duPont) U. S. 3,250,808 C.A. 65, 13554b
Fluorocarbon ethers from hexafluoropropylene oxide
- Mashburn, T. A. (to duPont) U. S. 3,257,466 C.A. 65, 13544e
Linear dimers of perfluoro(alkylvinyl ethers)
- Wall, L. A., Antonucci, J. M. (to U. S. Dept. of Navy) U. S. 3,265,746, C.A. 65, 13602b
Perfluorostyrene
- Warnell, J. L. (to duPont) U. S. 3,250,806, C.A. 65, 15230f
Fluorocarbon ethers of tetrafluoroethylene oxide
- Kresta, J., Ambroz, L., C.A. 65, 15514g
Study of the physiochemical properties of vinyl fluoride
- Pittman, A. G., et al., C.A. 65, 17056d
Polymers derived from fluoroketones. Preparation of fluoroalkyl acrylates and methacrylates
- Bergomi, A., et al., C.A. 65, 18504h
1H- and 2H-pentafluorocyclopentadiene
- Riera, J., Stephens, R., C.A. 65, 18506a
Fluorination of aromatic polyfluoro compounds. Could be used as a route to difficultly accessible polyfluoroolefins

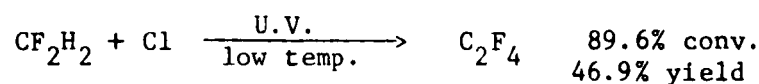
Eurant, E., et al., C.A. 65, 20000h
 α -Haloalkyl esters. $\text{RCO}_2\text{CHXR}'$

$\text{R} = \text{H, Me, CH}_2\text{X, CX}_3$

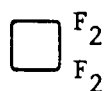
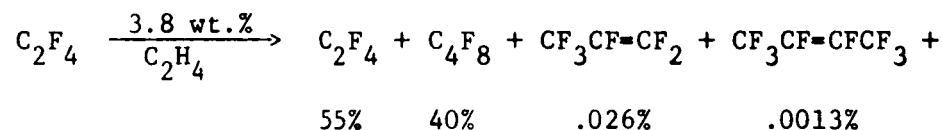
$\text{X} = \text{halogen}$

$\text{R}' = \text{H, Me, Et, iso. Pr}$

Mod, W. A., et al. (to Dow) U. S. 3,278,406, C.A. 65
 20004f

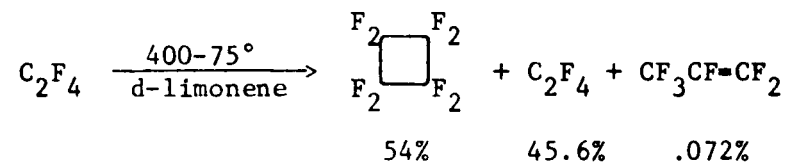


duPont, Neth. Appl. 6,607,056, C.A. 65, 20028f



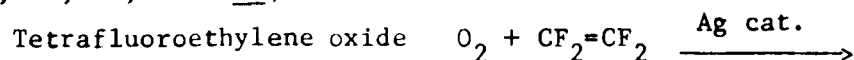
2.3%

duPont, Neth. Appl. 6,609,057, C.A. 65, 20028g



Selman, S. (to duPont) U. S. 3,274,239, C.A. 65, 20029a
 Perfluorocarbonyl compounds + perfluoropropylene oxide +
 $\text{RO}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{COF}$ $n = 0 \text{ to } 6$

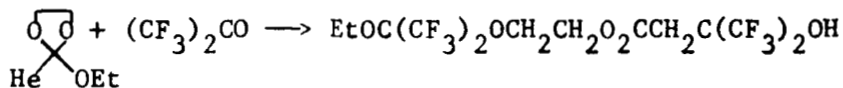
Societa Edison, S.p.A. -Settore Chimico, Neth. Appl.
 6,516,825, C.A. 65, 20099c



Butler, A. J., et al. (to Dow) Fr. 1,423,584, C.A. 65, 20243d
 Fluorinated monomers and polymers. Correction of
 pat. no. (C.A. 65, 17084h)

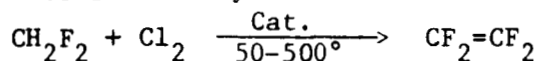
Braun, R. A., C.A. 66, 2008k

Reaction of hexafluoroacetone with orthoesters



Mod, W. A. (to Dow) U. S. 3,278,616, C.A. 66, 2182z

Tetrafluoroethylene from difluoromethane



Linn, W. J. (to duPont) U. S. 3,271,419

Fluoro-containing lactones and unsaturated acids

Banks, R. E., et al., C.A. 66, 2245p

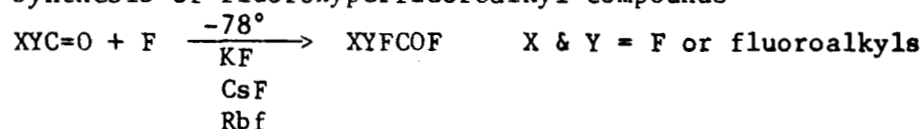
Polyhaloallenes. Thermal co-dimerization of tetrafluoroallene with hexafluorobut-2-yne

Banks, R. E., et al., C.A. 66, 2262q

Polyfluorocyclopentadienes. Thermal dimer of perfluorocyclopentadiene perfluoro(tricyclo[5.2.1.0^{2,6}]deca-3,8-diene)

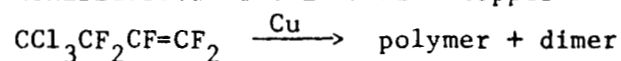
Ruff, J. K., et al.

Synthesis of fluoroxyperfluoroalkyl compounds



Mazalov, B. I., et al., C.A. 66, 10545n

Reaction of some derivatives of ω, ω, ω -trichloro-hexafluorovaleric acid with copper



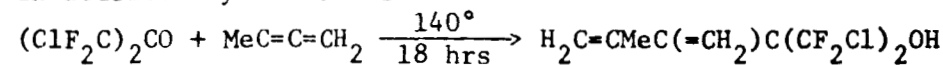
Lester, G. R., Adams, C. J. (Univ. Oil Prd. Co.)

U. S. 3,274,273, C.A. 66, 10551g

Dehydrohalogenation of halo hydrocarbons. Catalyst of oxide of Mg, Ca or Zn plus oxide Cu or Ce

Davis, H. R. (to 3M) U. S. 3,284,516, C.A. 66, 10568n

Reaction products of halogenated ketones with unsaturated hydrocarbons

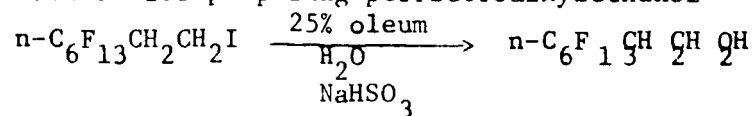


Warnell, J. L. (to duPont) U. S. 3,277,169, C.A. 66, 11304r

Fluorocarbon-hydrocarbon polyethers. Hexafluoropropylene oxide, or tetrahydrofluoroethylene epoxide with ethylene oxide, propylene oxide, oxetane or tetrahydrofuran

Gambaryan, N. P., et al., C.A. 66, 18477h
Reactions of the carbonyl group in fluorinated ketones.
A review

Day, R. I. (to duPont) U. S. 3,283,012, C.A. 66, 18507t
Process for preparing perfluoroalkylethanol



Fuller, G. (to Imperial Smelting Corp.) Brit. 1,047,318,
C.A. 66, 18585s
2-Pentafluorophenylethanol

VIII. Vulcanization of Fluorine-Containing Polymers

Lanza, V. L., Belg. 670,761, C.A. 65, 13925h
Vinylidene fluoride polymers cross-linked with trialkyl
cyanurate

Goldsmith (to Gen. Plastics Corp.) U. S. 3,281,511,
C.A. 66, 3358f
Process for increasing tensile strength and flexing
of poly(TFE)